Quantum-Tuned Multijunction Solar Cells

by

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Graduate Department of Electrical and Computer Engineering
University of Toronto

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Abstract

Multijunction solar cells made from a combination of CQDs of differing sizes and thus bandgaps are a promising means by which to increase the energy harvested from the Sun’s broad spectrum.

In this dissertation, we first report the systematic engineering of 1.6 eV PbS CQD solar cells, optimal as the front cell responsible for visible wavelength harvesting in tandem photovoltaics. We rationally optimize each of the device’s collecting electrodes—the heterointerface with electron accepting TiO$_2$ and the deep-work-function hole-collecting MoO$_3$ for ohmic contact—for maximum efficiency.

Room-temperature processing enables flexible substrates, and permits tandem solar cells that integrate a small-bandgap back cell atop a low thermal-budget larger-bandgap front cell. We report an electrode strategy that enables a depleted heterojunction CQD PV device to be fabricated entirely at room temperature. We develop a two-layer donor-supply electrode (DSE) in which a highly doped, shallow work function layer supplies a high density of free electrons to an ultrathin TiO$_2$ layer via charge-transfer doping. Using the DSE we build all-room-temperature-processed small-bandgap (1 eV) colloidal quantum dot solar cells suitable for use as the back junction in tandem solar cells.
We further report in this work the first efficient CQD tandem solar cells. We use a graded recombination layer (GRL) to provide a progression of work functions from the hole-accepting electrode in the bottom cell to the electron-accepting electrode in the top cell. The recombination layers must allow the hole current from one cell to recombine, with high efficiency and low voltage loss, with the electron current from the next cell.

We conclude our dissertation by presenting the generalized conditions for design of efficient graded recombination layer solar devices. We demonstrate a family of new GRL designs experimentally and highlight the benefits of the progression of dopings and work functions in the interlayers.
To my late grandmother Dado

The kindest, most loving, and simply the best person I have ever known
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<td>Colloidal quantum dot</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>DSE</td>
<td>Donor-supply electrode</td>
</tr>
<tr>
<td>GRL</td>
<td>Graded recombination layer</td>
</tr>
<tr>
<td>TW</td>
<td>Terawatt</td>
</tr>
<tr>
<td>GDP</td>
<td>Gross domestic product</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>AM1.5</td>
<td>Air mass 1.5</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Voltage at maximum power point</td>
</tr>
<tr>
<td>$J_m$</td>
<td>Current density at maximum power point</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
</tr>
<tr>
<td>DH</td>
<td>Depleted Heterojunction</td>
</tr>
<tr>
<td>DBH</td>
<td>Depleted bulk heterojunction</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron transporting layer</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole transporting layer</td>
</tr>
</tbody>
</table>

xxiii
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>FIB</td>
<td>Focus ion beam</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>FET</td>
<td>Field effect transistor</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>Molybdenum trioxide</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>AZO</td>
<td>Aluminum doped zinc oxide</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>S-TiO$_2$</td>
<td>Shallow electron affinity TiO$_2$</td>
</tr>
<tr>
<td>M-TiO$_2$</td>
<td>Medium electron affinity TiO$_2$</td>
</tr>
<tr>
<td>D-TiO$_2$</td>
<td>Deep electron affinity TiO$_2$</td>
</tr>
<tr>
<td>S-AZO</td>
<td>Shallow electron affinity AZO</td>
</tr>
<tr>
<td>M-AZO</td>
<td>Medium electron affinity AZO</td>
</tr>
<tr>
<td>IL</td>
<td>Intervening layer</td>
</tr>
<tr>
<td>OE</td>
<td>Ohmic electrode</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

“Energy is the single most important challenge facing humanity today”

—Nobel Laureate Rick Smalley, April 2004, Testimony to U.S. Senate

1.1. The Energy Problem

Energy is the currency of the world; it is one major determining factor of the prosperity of any society.¹ We depend on various forms of energy in every aspect of our daily lives. Without energy, we are crippled: we cannot drive cars, operate machines, have easy access to water and food or even see after dark. It is also one of the leading catalysts of global conflicts.²³ All challenges facing humanity from hunger and war to environment and population growth would be easier solved with cheap and accessible energy.¹³

1.1.1. The Terawatt Challenge¹

The current world global energy consumption, evaluated as the number of Joules of energy consumed in a year divided by the number of seconds in a year, is about 15 trillion watts or terawatts (TW).⁴ Figure 1 is a photo of the world’s nightlights.⁵ The brightest areas, the United States and Western Europe, are not the most populous world regions.⁶

Figure 1 Earth’s Nightlights (NASA Image 2011).⁵ The brightest areas do not correspond to the most populous countries.
There is a great number of people who do not currently have access to electricity and global population is projected to grow to 10 billion people by 2050.\textsuperscript{2,3} Taking into account the gross domestic product (GDP) growth reaching over 10\% in several populous countries as depicted in Figure 2,\textsuperscript{6} the energy demand is going to at least double\textsuperscript{3} by 2050. This estimation factors in optimistic assumptions about increased energy efficiency.

Figure 2 World GDP growth rate (\%). Countries with large population such as China and India will want to increase their energy use.\textsuperscript{6}

1.1.2. Energy Sources

Eighty-five percent of the 15 TW present-day energy demands are satisfied by fossil fuel energy (Table 1) with renewable energy only representing around \(\sim 9\%\) of the total energy consumption with hydroelectric power and biomass comprising \(\sim 8\%\).\textsuperscript{3} Table 1 summarizes the average cost of electricity production from various sources.\textsuperscript{3,7}

Table 1 Global energy consumption distributed by resource; the average cost of electricity production from those resources is included in cents/kWh.

<table>
<thead>
<tr>
<th>Energy Source</th>
<th>Global Power Consumption (%)</th>
<th>Cost (Cents/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas</td>
<td>23</td>
<td>2.5-5</td>
</tr>
<tr>
<td>Coal</td>
<td>25</td>
<td>1-4</td>
</tr>
</tbody>
</table>
Fossil fuels cannot remain the world’s main source of energy for long because they are going to be depleted eventually and with the decrease of resources, prices will soar and further global geopolitical conflicts will arise. The state of the global energy consumption will then shift towards a more prominent contribution from renewable energies.

1.1.2.1. Carbon Dioxide Production

Carbon dioxide (CO₂) is an end product produced when fossil fuels are burned. It is released into the atmosphere with a long lifetime and no means of fast natural decomposition: thirty years of accumulated CO₂ emissions will not dissipate for over centuries. There lies another major aspect in the energy problem. With the increase of fossil fuel energy use, the cumulative CO₂ levels have reached unprecedented levels (>350 parts per million by volume or ppmv) in thousands of years (Figure 3).  

<table>
<thead>
<tr>
<th>Energy Source</th>
<th>CO₂ Emissions</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>37</td>
<td>6-8</td>
</tr>
<tr>
<td>Nuclear</td>
<td>6</td>
<td>6-7</td>
</tr>
<tr>
<td>Hydro</td>
<td>3</td>
<td>5-11</td>
</tr>
<tr>
<td>Biomass</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Wind</td>
<td>0.6</td>
<td>4-6</td>
</tr>
<tr>
<td>Solar</td>
<td>0.5</td>
<td>25-50</td>
</tr>
<tr>
<td>Geothermal</td>
<td>0.4</td>
<td>5-30</td>
</tr>
</tbody>
</table>

CO₂ levels are expected to rise above 550 ppmv in 2050 which will have devastating consequences on the world; we are already experiencing massive climate changes, and rising ocean levels and doing nothing to halt the rise of CO₂ levels will accentuate the problem.
Figure 3 Atmospheric greenhouse gas concentrations from ice cores drilled at Vostok, Antarctica compared with the average temperatures. Adapted with permission from Macmillan Publishers Ltd: Nature© copyright 1999.

From Figure 3, the CO\(_2\) concentration is directly correlated with the average temperatures. With the accumulation of atmospheric CO\(_2\) emissions above normal values, the earth average temperature is also on the rise and is widely believed to be the cause of the melting of Greenland’s ice sheet. Furthermore, permafrost frozen for over 40 000 years is melting, releasing massive amounts of trapped greenhouse gases.\(^3\) There is a need for an aggressive deployment of carbon-free energy that will help stabilize the CO\(_2\) levels.

1.1.2.2. Carbon-free Energy Resources

Nuclear energy is a carbon-neutral proven and scalable technology; there are currently 400 one-gigawatt nuclear power plants deployed around the world. In order to reach the TW challenge by 2050, we would need about 10 000 reactors built. In fact, with their commissioned lifetime being only 50 years, we would need to be continuously building reactors. Thus, nuclear option would only be a possibility if fast-breeder technology is developed.\(^3\) Furthermore, nuclear waste disposal remains a challenge.

Hydroelectric power is one of the oldest forms of renewable energy but practically, only about 1.5 TW could be generated because hydro plants can only be built in a limited number of locations. Wind is one of the cheapest renewable energies available but many factors, such as the wind farms’ high mechanical fatigue failure, and their inability to function in rainy, cold
climates, are limiting its widespread. In addition, they are very noisy, and cannot be insulated to reduce the noise because of the resulting loss in efficiency. They are thus usually geographically limited to remote non-residential areas. The practical energy available from wind energy is estimated to be 2-4 TW, still not enough to satisfy our future energy needs on its own.

Geothermal would become more substantial if low temperature conversion of heat to electricity becomes efficient, rendering it less expensive due to the shallow drilling becoming possible. Furthermore, the lifetime of deep geothermal wells in hot dry rocks is only 5 years. Another renewable energy is biomass but due to its inefficiency (0.3%), it requires large land areas to be relevant. Taking into account the population growth, and the available land area, biomass is estimated to be able to provide 5-7 TW of energy.\textsuperscript{1,3}

Among all the carbon-free energy solutions discussed above, solar conversion is definitely the most expensive energy resource at the present time; however, it has the largest potential out of all renewables.

### 1.2. Solar Energy

120 000 TW of radiant energy reaches the earth’s surface from the sun. Solar energy is the only abundant resource that could satisfy on its own the growing global energy demands; no other resource comes close. In fact, in one hour, the sun provides the planet with more energy than the global energy consumption in one year.\textsuperscript{1,3} Table 2 summarizes the various carbon-free energy resources practical energy potential and their current level of use in TW. Taking into account a 10% conversion efficiency, the solar technical potential is equivalent to 60 TW, which is large enough to satisfy future energy demands.\textsuperscript{3}
Table 2 Summary of carbon-free energy sources, their global potential and current use

<table>
<thead>
<tr>
<th>Energy Source</th>
<th>Practical Potential (TW)</th>
<th>Current Level (TW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroelectric</td>
<td>1.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Geothermal</td>
<td>11.6</td>
<td>0.07</td>
</tr>
<tr>
<td>Wind</td>
<td>2-4</td>
<td>0.09</td>
</tr>
<tr>
<td>Biomass</td>
<td>7-10</td>
<td>0.75</td>
</tr>
<tr>
<td>Solar</td>
<td>600</td>
<td>0.08</td>
</tr>
</tbody>
</table>

1.2.1. Land Area Considerations

Powering the world today would only require six 400 by 400 km pieces of land in sunny areas across the globe stacked with 10% efficient solar panels. Figure 4 is an illustration of the land requirement to satisfy the global annual energy consumption today with each box representing ~3 TW.  

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1. This line is numbered as 1, suggesting it's the first part of a series or section. It would be more contextually clear if it were not numbered at this point.
1.2.2. Cost vs. Efficiency

The main obstacle standing in the way of global deployment of solar panels to produce electricity is its current high cost ranging from 25 to 50 cents per kilowatt-hour. The cost of the system is not entirely derived from the manufacturing expenses but rather from storage, installation, maintenance, among other balance of system costs that accumulate over the lifetime of the module. Advances have been achieved in increasing the efficiency of solar cells employing costly monocristalline materials and complicated architectures utilizing epitaxially-grown multijunction technology. There is a strong need to develop efficient, cheap and scalable solar technologies that can be stored at fraction of the current cost.

1.2.2.1. Solution-Processed Photovoltaics

In the last decade research efforts explored promising inexpensive materials in efficient solar applications. Solution-processed active materials have a great potential in this regard. The ability to deposit those materials via drop-casting, blade coating, spray-coating or ink-jet printing enabling roll-to-roll fabrication renders them extremely attractive.
Solution-processed solar cells are lightweight, flexible, scalable, low-temperature processed, inexpensive\(^{10,11}\) and research targeted at increasing their efficiencies have been showing great momentum in recent years.\(^{12}\) These include dye-sensitized solar cells (DSSC),\(^{13}\) organic photovoltaics,\(^{14}\) solution-processed bulk inorganic photovoltaics,\(^{15}\) and colloidal quantum dot solar (CQD) cells.\(^{11}\) While DSSCs have surpassed 10% efficiency in the 1990’s, organic photovoltaics since their first report more than two decades ago have surpassed 5% only in 2006 and very recently reached 10% in their tandem and single architectures.\(^{12,16}\) Similarly, bulk inorganic photovoltaics (CIGS and CZTS) only recently reached 10% through advances in material processing.\(^{15}\)

On the other hand, CQD photovoltaic research still in its infancy has since its emergence in 2005\(^ {17,18}\) reached 7% efficiency in 2012.\(^{19,20}\) With their unique ability to easily access and thus harness different regions of the solar spectrum from the visible to the far-infrared, inherent of their quantum confinement, semiconducting colloidal quantum dot materials are promising candidates for photovoltaic applications.\(^ {11,17,21}\)

### 1.3. Thesis Objectives

At the start of this thesis in 2008, CQD solar research was still in its early conception. Single junction device architectures have progressed from Schottky junctions\(^ {22,23}\) to depleted heterojunctions.\(^ {24}\) This thesis takes advantage of the CQD single junction architecture advancements and explores multijunction designs that have not been previously explored in CQD material systems. This work focuses on answering the following key research objectives:

1. **Efficient use of the CQD spectral tunability.**

Through the size-tuning of CQD, different regions of the sun’s spectrum can be harnessed. In CQD optoelectronics, multijunctions employing different CQD bandgaps have not been reported before this work; the optimal bandgaps of a CQD tandem solar cell are 1.6 and 1 eV. Is it possible to fabricate efficient photovoltaic devices of varying size to achieve selective spectral tunability? Will we need to conduct material processing modifications for the different sizes? Will those modifications render them incompatible for monolithic integration?
2. Designing efficient front and back single junctions to be integrated in CQD tandem solar cells.

The first consideration we accounted for in this work is our choice of optimal bandgap for tandem junction to enable maximum power efficiency through optimal current matching conditions. Never before our work has a visible 1.6 eV efficient PbS CQD solar cell, i.e. the front cell of a tandem junction, been reported. What are the design specifications we need to consider to maximize electron injection from the 1.6 eV PbS CQD without compromising the open circuit voltage of the solar cell? Furthermore, all single junctions before the conception of this work were fabricated on high-temperature processed electrodes (>500°C) incompatible with CQD tandem junction integration. How would the inclusion of an infrared 1 eV layer be possible atop the front cell of a tandem structure? Would a simple replacement of the electron accepting electrode with its room-temperature processed counterpart lead to efficient devices?

3. Fabrication of the first CQD tandem solar cell.

The main challenge was connecting the front and back cells with a recombination layer that was compatible – in its materials processing – with each quantum dot layer. This is achieved using tunnel junctions in epitaxial compounds and water-processed recombination layers in organic photovoltaics; both these strategies are not viable for CQD processing. How can we build a recombination layer that efficiently brings the electrons from the back cell to the holes from the front cells without loss and that is at the same time room-temperature CQD processing compatible?

4. Designing efficient graded recombination layers for multijunction photovoltaics.

Employing the graded recombination layer (GRL) in our tandem solar cells led us to question the general design requirements for an efficient GRL in multijunction photovoltaics. This analysis would potentially benefit the growing research directed into solution-processed multijunction structures. What are the electrical properties, i.e. work functions and doping densities, of the interlayers included in the GRL that would enable us to achieve low absorbance and photovoltage loss while still sustaining solar intensities?
All the above questions will be answered in this dissertation.

1.4. Thesis Outline

The following chapters of this thesis will be organized as follows:

Chapter 2 describes relevant photovoltaic concepts. We start by examining the spectrum of the solar radiation arriving at the surface of the earth and continue by explaining all the processes that occur once an active layer of a photovoltaic device absorbs photons and result in the generation of an electric current. We proceed by defining all the figures of merit needed to evaluate the performance of a solar cell. The requirement for an ideal solar cell is then discussed and the chapter concludes by elucidating the limits of energy conversion and the optimal bandgaps for single and multijunction photovoltaics.

We sought to review the preexisting literature concerning CQD photovoltaics (PV) in chapter 3. We start with briefly describing the attractive properties of CQD materials and then describing the important architectures employed in CQD PV thus far. The Schottky junction is the structure adopted in the early years of CQD PV while the depleted heterojunction is currently widely employed. We conclude the chapter by presenting the motivation behind building CQD tandem solar cells.

In chapter 4, we present the experimental methodology employed in this work. We first describe the synthesis and solution processing of the CQD material we employ followed by a description of film deposition and device fabrication. We also explain the various material characterization techniques we use in order to elucidate optical, electrical and film properties. We then discuss the device testing setups that allows us to evaluate the performance of the devices.

We start in chapter 5 discussing the methodology we employed in designing efficient visible and infrared single junctions. We discuss the design requirement of the electron accepting electrode and ohmic contact for an efficient 1.6 eV single junction and the room-temperature strategy we used to fabricate an infrared junction capable of being integrated in a tandem junction.

In chapter 6, the world’s first CQD tandem solar cell is presented; we discuss the recombination layer design we conceived compatible with CQD room-temperature processing. We discuss how
we were able to achieve current matching in our series connected tandem solar cell and introduce the properties of the different materials used within the graded recombination layer.

We describe in chapter 7 the design requirements necessary to design efficient graded recombination layer for multijunction photovoltaics. We determine the number of interlayers required, their work function and doping densities enabling solar intensities across work function difference as high as 1.6 eV at minimal photovoltage loss.

The dissertation concludes with a description of research contributions and a discussion of future prospects in CQD photovoltaic design.
Chapter 2 Solar Photovoltaics

We established in chapter 1 the attractiveness of solar energy and particularly the use of solution-processed colloidal quantum dots in photovoltaic applications. Photovoltaic conversion is an elegant one step process where incoming optical power is converted to electrical power. This chapter aims to lay out briefly the pertinent theoretical concepts relating to the photovoltaic effect. First, we discuss the solar resource and the properties of the radiant energy the earth receives. This is followed by a description of the characteristics of the photovoltaic cell and the different relevant figures of merit. At the conclusion of this chapter, the requirements for the ideal photoconverter are presented.

2.1. The Solar Resource

The sun’s radiant energy reaches the earth with a range of wavelengths spanning the ultraviolet (UV), the visible and the infrared regions (IR) of the spectrum. One half of the solar radiation is concentrated in the visible while the other half of the sun’s energy lies in the infrared section. In order to evaluate solar cells, the Air Mass 1.5 is utilized as the standard solar spectrum.

2.1.1. Air Mass 1.5

The solar irradiance, i.e. the amount of radiant energy received from the sun per unit area per unit time, as a function of wavelength is absorbed and scattered by a multitude of atmospheric constituents. Thus, atmospheric absorptions attenuate and produce a number of sharp dips within the solar spectrum. Ozone, oxygen and nitrogen are highly absorptive in the UV range (<300 nm) and consequently filter out the high energy portion of the solar spectrum. Characteristic absorption by H₂O and CO₂ produce a number of distinctive dips within the infrared portion of the solar spectrum.

The extent to which the solar spectrum is absorbed by the atmosphere is dependent on the path length of the sun’s rays passing through the atmosphere; the latter is directly related to the angle of inclination of the sun with respect to the earth’s surface. The path length of the sun’s rays through the terrestrial atmosphere is quantified by an “Air Mass” factor defined by the following equation.
Figure 5 depicts the solar spectra in space termed AM0 in comparison with the standard solar spectra adopted for terrestrial applications, the AM1.5 spectra. The pathlength factor of AM1.5 is consistent with an angle of inclination of 42°.

2.2. Solar Energy Conversion

The photovoltaic effect is an energy conversion process that produces electrical energy from incident light energy. It involves the following steps illustrated in Figure 6:

1) Absorption of photons and formation of an electron-hole pair
2) Carrier separation

3) Carrier transport

4) Carrier extraction

Figure 6 Photovoltaic energy conversion process. The photon is initially absorbed resulting in the excitation of an electron-hole pair; the carriers are then separated by a built-in driving force, transported through the medium and finally collected.

Absorption of a photon in a material causes the excitation of an electron to a higher energy state leaving a hole behind in the ground state. Only photons with enough energy to surpass the bandgap separation can be extracted in a solar cell. For efficient charge separation, a built-in asymmetry is needed to drive the carriers away from their point of creation before they recombine. Various charge separation mechanisms exist and the ones relevant to our work will be further discussed in chapter 3. Once separated, the carriers are transported within the material with minimal loss; thus, higher carrier mobility and minimal recombination centers are attractive. Finally, the carriers are extracted to the external circuit by appropriately selected contacts.²⁶

2.3. Circuit Model

A solar cell can be modeled as a current generator in parallel with a diode (Figure 7). The current source represents the photocurrent produced by the cell and is divided between the diode and the load while the diode provides the photovoltage.²⁶
2.4. Definitions

In this section, we layout the theoretical concepts relating to the different pertinent figures of merit employed in our experimental work.

2.4.1. Absorption Coefficient

We already established that a semiconductor only absorbs photons with energies higher than their bandgap in the previous section. As the thickness of the absorbing layer is increased, more of the incident photons are absorbed. This is empirically indicated by the drop in light intensity as the light propagates through a medium according to the following Beer-Lambert law:\textsuperscript{28}

\[
I(z) = I_0 \exp(-\alpha z) \tag{Equation 2}
\]

where \(I(z)\) is the intensity of light in the material at distance \(z\), \(I_0\) is the incident light intensity and \(\alpha\) is the absorption coefficient unique to the material. When the thickness of the absorbing layer in a solar cell is increased beyond a certain thickness, carrier recombination becomes dominant and the power conversion efficiency of the solar cell suffers. Thus, the electrical transport characteristics of the medium in addition to its optical properties are of equal importance for efficient photovoltaic conversion.\textsuperscript{9,26,28}
2.4.2. Short Circuit Current Density and Open Circuit Voltage

The short circuit current ($I_{sc}$) is the current generated when the terminals of the solar cells are shorted: it is the maximum amount of current that is produced by a solar cell. The short circuit current density ($J_{sc}$) is expressed in mA/cm$^2$.

The solar cell behaves as a diode in the dark where the current is very large in the forward bias mode compared to negligible current in the reverse bias region.\(^{28,29}\) The current flowing through a solar cell can thus be expressed as

$$J_{\text{dark}} = J_0 \left( e^{\frac{eV}{kT}} - 1 \right) \text{ Equation 3}$$

where $J_0$ is the saturation current density. Lowering the saturation current density, which usually is derived from parasitic losses and serves to oppose the photogenerated current, is essential in efficient solar cells.

Under illumination, a photocurrent is produced which is opposite in direction to the dark current and current expression becomes

$$J(V) = J_{sc} - J_{\text{dark}}(V)$$

$$\Rightarrow J(V) = J_{sc} - J_0 \left( e^{\frac{eV}{kT}} - 1 \right) \text{ Equation 4}$$

Equation 4 is an ideal representation of the current density. In reality, an ideality factor $m$ (1< $m$ < 2) is included in the expression which becomes\(^{26}\)

$$\Rightarrow J(V) = J_{sc} - J_0 \left( e^{\frac{eV}{m_kT}} - 1 \right) \text{ Equation 5}$$

The open circuit voltage ($V_{oc}$) is the voltage generated when the terminals of the solar cell are isolated. It is the maximum produced voltage in a solar cell. The expression for the $V_{oc}$ is derived directly from Equation 5 for total current $J(V)$ equal to 0 and is expressed as

$$\Rightarrow V_{oc} = \frac{kT}{q} \ln \left( \frac{J_{sc}}{J_0} + 1 \right) \Rightarrow V_{oc} = \frac{m k T}{q} \ln \left( \frac{J_{sc}}{J_0} + 1 \right) \text{ Equation 6}$$
It is worthy to note that the $V_{oc}$ is proportional to the logarithm of the ratio of $J_{sc}$ to $J_0$: thus, as the saturation current increases, $V_{oc}$ will drop substantially.

Solar cell materials with high $J_{sc}$ tend to have lower $V_{oc}$, inherent of the semiconductor bandgap; with larger bandgap, the $V_{oc}$ increases but the amount of photons to be absorbed and converted to current decreases.

### 2.4.3. Fill Factor and Power Conversion Efficiency

Figure 8 summarizes the relevant figures of merit of a solar cell in a J-V curve. The fill factor ($FF$) describes how closely the maximum power point ($V_m, J_m$) coincides with $V_{oc}$ and $J_{sc}$ and is expressed as

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \quad \text{Equation 7}$$

If the J-V curve is a perfect square, $FF$ would be unity. However, in practical applications, a solar cell is always susceptible to parasitic resistive losses directly affecting the $FF$.

![Figure 8 J-V curve of a solar cell with all the relevant figures of merit.](image-url)
The most relevant figure of merit is the power conversion efficiency (PCE) of a solar cell and is a measure of the fraction of input light power that is converted to electrical power. The PCE is expressed as

\[
\eta = \frac{J_m V_m}{P_i} = \frac{J_{sc} V_{oc} FF}{P_i}
\]  
\text{Equation 8}

where \(P_i\) is the incident light power.

In 1961, Shockley and Queisser determined that the detailed balance power conversion efficiency is limited to 33% for single junction solar cells under unconcentrated AM1.5 illumination conditions corresponding to an optimal single junction bandgap of 1.3 eV.

2.4.4. External and Internal Quantum Efficiency

Quantum efficiency is the probability that an incident photon will deliver a single electron to the external circuit. It is essentially the number of electrons generated per photon and therefore it is unit-less. Quantum efficiency is a function of the photon energy and is dependent on the absorption coefficient of the material and the charge separation and collection efficiencies of the solar cell.

The external quantum efficiency (EQE) is expressed as

\[
\eta_{\text{ext}} = \frac{I_{sc}}{I_{ph}}
\]  
\text{Equation 9}

where \(I_{ph}\) is the current that would result if all incident photons (with energy \(E > E_g\)) created electrons that contributed to the external current. The EQE spectrum in conjunction with the AM1.5 spectra is often utilized to determine the total current density expected to be generated from the solar cell.

The internal quantum efficiency (IQE) is expressed as

\[
\eta_{\text{int}} = \frac{I_{sc}}{I_{gen}}
\]  
\text{Equation 10}
where \( I_{gen} \) is the current that would result if all absorbed photons created electrons that contributed to the external current. The IQE basically only takes into account the photons absorbed in the material and hence practically will be always larger than the EQE.\(^9\) The IQE is a strong indication of how efficient the charge separation, transport and extraction are in the solar cell.

### 2.4.5. Series and Shunt Resistance

In real solar cells, parasitic losses decrease the PCE of the solar cell. These can be modeled in the circuit model as parasitic resistances which are connected in series (\( R_{\text{series}} \)) and in parallel (\( R_{\text{shunt}} \)). Series resistance manifests as resistance to the current flow in the cell as contact resistance, and low carrier mobility in the material; on the other hand, shunt resistance is due to alternative current paths in the device such as soft shorts, and recombination centers. Both resistances directly affect the fill factor of the device as depicted in Figure 9 a and b.
In an efficient solar cell, the series resistance is small while the shunt resistance is large. When parasitic resistances are included in the analysis, the diode equation becomes

\[ J = J_{sc} - J_0 \left( e^{q(V + JAR_s)/kT} - 1 \right) - \frac{V + JAR_s}{R_{sh}} \]  

Equation 11

2.5. The Ideal Photoconverter

Taking into consideration all the figures of merit described above, the characteristics of the ideal solar cell can be deduced:

1) It must have a high \( J_{sc} \), a high \( V_{oc} \), and a \( FF \) close to unity

2) \( J_{sc} = \text{IQE} \times I_{gen} \) is directly dependent on the amount of light absorbed and on the internal collection efficiency which in turn is dependent on the recombination processes inside the solar cell. Thus an ideal solar cell will have minimal recombination losses, minimal reflection losses at the interface, and it must be thick enough to absorb all the incoming light.

3) Minimizing the saturation current as previously mentioned increases both \( V_{oc} \) and \( FF \).
In short, the optimal design of a solar cell must aim to (1) minimize loss mechanisms throughout the device and (2) maximize light absorption.

2.6. Solar Energy Conversion Limits

As previously mentioned, efficiency is the important figure of merit when it comes to assessing the performance of a solar cell. The efficiency is strongly related to the generation of electron-hole pair inside the material and the limit of their recombination before being extracted to the external circuit. In 1961, Shockley and Queisser determined that the unavoidable recombination mechanisms were just part of the detailed balance model.\textsuperscript{30} They determined the maximum efficiency expected from a solar cell, which we will briefly present here.

2.6.1. Thermodynamic Limits to Energy Conversion

Considering the solar radiation can be approximated by a blackbody spectrum at a 6000 K temperature, and assuming that the solar cell absorbing the solar energy is at room temperature of 300 K, the Carnot efficiency is

$$\eta_{\text{Carnot}} = 1 - \frac{T_{\text{low}}}{T_{\text{high}}} \approx 95\%$$  \hspace{1cm} \text{Equation 12}

Considering entropy, i.e. the energy lost via heat generation, the efficiency becomes lower\textsuperscript{31}

$$\eta_{\text{max,Entropy}} = 1 - \frac{4}{3} \frac{T_{\text{low}}}{T_{\text{high}}} \approx 93\%$$  \hspace{1cm} \text{Equation 13}

In principle, the efficiency of a cell can be brought close to this limit by using concentrators of radiation. For a regular planar cell without concentrators, the limiting approachable efficiency is much lower and obtained from the detailed balance model.

2.6.2. Detailed Balance Model

Shockley and Queisser were the first to consider the detailed balance limit of solar cell efficiency. In 1961, they realized that within the detailed balance model the current flowing out of the device is the difference between the radiation absorbed and the amount of radiation emitted.\textsuperscript{30} The following are the remaining assumptions in the detailed balance model:
• The only recombination process is radiative recombination.

• All photons with energies larger than the bandgap of the material is absorbed and all photons below the bandgap are not.

• The difference in quasi-Fermi levels is the same where the photocarriers are generated and extracted.

• Each photon absorbed generates one electron-hole pair.

The complete analysis of Shockley and Queisser predicts that for a single junction the efficiency maximum is ~31% corresponding to an optimal bandgap of 1.3 eV.\textsuperscript{25,30}

2.6.2.1. Graphical Representation

Calculations of the efficiency of single and multiple junction solar cells are made simpler with the utilization of graphical method.\textsuperscript{31} In this analysis, the blackbody spectrum is replaced by the standard AM1.5. Assuming all photons with energies less than the bandgap are absorbed, the integration of the spectrum is carried out to determine the absorbed solar flux ($n_{ph}(E_g)$, in photons cm\textsuperscript{-2} sec\textsuperscript{-1}) (Figure 10). The work done per absorbed photon (W) is also depicted in Figure 10: taking into account the radiative current component, W is usually about 0.4 to 0.5 eV less than $E_g$. The highest efficiency of 31% is obtained for $E_g = 1.34$ eV (Figure 10a).\textsuperscript{31}
Graphical analysis of the optimal bandgap (s) of a (a) single and (b) tandem solar cell. The bandgap $E_g$ (black) and the work done per absorbed photon (red) as a function of the solar flux ($n_{\text{photon}}$) are depicted. Three intrinsic losses are depicted: the photons with $h\nu < E_g$ are not absorbed, photons with $h\nu > E_g$ lose all energy in excess of $E_g$, and the radiative recombination loss limiting the work done per photon $W$.\textsuperscript{31}

The optimal bandgaps of a series connected tandem junction can be easily obtained employing the above graphical analysis by defining that the current generated by each individual junction ($E_{g1}$ and $E_{g2}$) is equivalent (Figure 10b). The optimal bandgaps obtained are 1.6 and 0.94 eV for current-matched tandem junction.\textsuperscript{25,30,31}
2.7. Summary

This chapter provided the relevant concepts relating to photovoltaic conversion.

A semiconductor absorbs photons of energy larger than its bandgap. The sun’s spectrum ranges from the UV to the IR with the half of it residing in the infrared; thus, the optimal bandgap of a single junction and the back cell of a tandem must lie in the infrared. The thicker the active material is the more photons it can absorb.

When a photon is absorbed an electron-hole pair forms; due to a built-in asymmetry in the solar device, charge separation occurs followed by electrons and holes transported in different directions. Finally, the carriers are collected through their respective contact.

We defined important figures of merit in this chapter which include the short circuit current, the open circuit voltage, the fill factor, the power conversion efficiency, the external quantum efficiency and the internal quantum efficiency.

We finally established that designing an ideal photoconverter requires minimizing the parasitic and recombination losses throughout the device and maximizing the light absorbed in the active region of the device.

In the following chapter, we present the recent reported progress in CQD photovoltaics. We include a brief description of the CQD properties and attractive features, the relevant single junction architectures and achieved performances, and we conclude with our motivation for building a tandem CQD solar cell.
Chapter 3 Colloidal Quantum Dot Photovoltaics

The previous chapter described the fundamentals of photovoltaic conversion. We now turn to position our work within the context of published reports in colloidal quantum dot photovoltaics. We first examine the properties of colloidal quantum dots and then follow by presenting the different photovoltaic architectures employing colloidal quantum dots. We present the motivation for our work on colloidal quantum dot multijunction at the end of this chapter.

3.1. Colloidal Quantum Dots Properties

Employing CQDs in photovoltaic applications enables the effective use of the sun’s entire spectrum (Figure 11a). CQDs are semiconductor nanoparticles synthesized in oxygen and moisture-free Schlenk line (Figure 11b) and subsequently deposited into thin films through various solution processing fabrication methods (Figure 12).11,17,32,33

Figure 11 (a) Size tunability of PbS colloidal quantum dots. Reprinted with permission from Macmillan Publishers Ltd: Nature Photonics11 copyright 2012 (b) Schlenk line for PbS quantum dots used in our labs.
Figure 12 Solution processibility of CQDs deposited into thin films by multiple fabrication processes. In our lab, spin-coating is widely used. Reprinted with permission from Macmillan Publishers Ltd: Nature Photonics 11 copyright 2012.

When the dimensions of the nanoparticle are reduced below the electron Bohr radius of the material, the continuous energy bands of the bulk material become discrete energy levels (Figure 13). The electronic excitations become deeply affected by the particle boundaries. The absorption spectrum becomes easily tunable through this effect as seen in Figure 11a. Through simple modifications to synthesis conditions, quantum size-tuning is enabled allowing easy access to the different portions of the solar spectrum ranging from the visible to the near-infrared.
In particular, lead salt quantum dots unlike other materials enable the regime of extreme quantum confinement. Their large Bohr radii allow strong confinement to occur in larger nanoparticles; the quantum confined lead salt colloidal quantum dots can be easily engineered to access far into the infrared region. PbS colloidal quantum dot’s minimal transitional energy is given by the PbS bulk bandgap of 0.41 eV.

3.2. Colloidal Quantum Dot Photovoltaics

Since the first report of PbS colloidal quantum dot solar cells in 2005, vast progress has been made towards higher efficiency CQD solar architectures. Multiple device architectures, such as metal/CQD film, oxide/CQD film, organic polymer layer/CQD film, and CQD film/CQD film have been explored in recent years. The latest published reports show single junction employing PbS CQD already reaching 6% PCE; Figure 14 depicts the rapid progress of CQD photovoltaics. In the following sub-sections, we briefly review the progress in Schottky and depleted heterojunctions employing colloidal quantum dots.
Figure 14 Progress in efficiency of CQD photovoltaics employing Schottky and depleted heterojunction architectures. Reprinted with permission from Macmillan Publishers Ltd: Nature Photonics\textsuperscript{11} copyright 2012.

3.2.1. CQD Schottky Junction

This section first provides a succinct description of Schottky junction physics followed by a layout of the recent progress in CQD Schottky junction architectures.

3.2.1.1. Schottky Junction Barrier

A Schottky barrier forms when a doped semiconductor is brought into contact with a metal.\textsuperscript{29} Figure 15a illustrates a p-type semiconductor of work function $\phi_p$ and electron affinity $X$ and a shallow work function ($\phi_m$) metal contact isolated from each other. When they come into contact, the Fermi levels line up under equilibrium conditions (Figure 15b).
Figure 15 Band diagram of a p-type Schottky junction (a) when the semiconductor and metal contact are isolated from each other and (b) after contact under equilibrium conditions.

Upon contact, carrier redistribution occurs at the interface until equilibrium is reached and a space charge region, i.e. depletion region, is created inside the p-type semiconductor. The semiconductor energy bands bend and a built-in field is established across the depletion region.\textsuperscript{29} In this structure, the field inside the depletion region is responsible for charge separation and the electrons are injected into the metal while the holes are repelled from the rectifying electrode. Schottky junctions practically suffer from high reverse saturation current density and from Fermi level pinning at the metal-semiconductor interface due to trap states, both detrimental to \( J_{sc} \) and \( V_{oc} \) respectively.\textsuperscript{32}

### 3.2.1.2. Progress in CQD Schottky Junction Photovoltaics

The first colloidal quantum dot based solar cell to reach 1% efficiency was a Schottky architecture.\textsuperscript{22,23} In this architecture, a transparent conducting oxide with a deep work function, i.e. indium tin oxide (ITO), was employed as the ohmic contact with the p-type PbS film. A shallow work function metal such as Al or Mg was used to form the rectifying junction. In those devices, transport lengths in the range of 10-100 nm were observed. While absorption increased for films of over 200 nm, carrier generated too far from the junction experienced recombination resulting in reduced collection efficiency.\textsuperscript{22,23} Figure 16 is an illustration of a CQD based Schottky junction and its band diagram at equilibrium and under illumination conditions.
Progress has been made over the last 4 years in CQD Schottky junctions mainly due to the improvement in the electrical properties of the CQD film. Various chemical solid-state treatments, mainly aimed at reducing the inter-nanoparticle distances, were employed in those structures; carrier mobility in those treated CQD films vastly improved leading to a PbSe CQD Schottky cell record efficiency of 4.6%.

3.2.2. CQD Heterojunction Photovoltaics

While the Schottky junction is simple to realize, it is strongly limited by the thickness of the PbS film: illuminating from the ohmic side, the carriers generated far from the rectifying electrode need to be transported over 100 nm thickness to the depletion width where they are swept away. These carriers are subject to recombination in view of the limited minority carrier diffusion in the CQD films. Increasing absorption to improve the photogenerated current cannot be achieved with this structure. Furthermore, the $V_{oc}$ is limited by Fermi-level pinning at the semiconductor-metal interface. In this section, we layout the theoretical concepts behind homojunctions and heterojunctions followed by the progress made with the following structures: electron donor organic/n-type CQD, n-type CQD/p-type CQD, and finally n-type wide bandgap semiconductor/p-type CQD.
3.2.2.1. Semiconductor-Semiconductor Junctions

When bringing an n-type semiconductor in contact with a p-type semiconductor, and due to the large concentration gradient, electrons diffuse from the n to the p-side while holes migrate from the p to the n-side. Positive charges left in the quasi-neutral region of the n-type material now depleted from its electrons create a built-in electric field; similarly, negative charges on the p-side establish an internal field in the quasi-neutral region in the p-type material. The resultant electric field opposes the gradient-driven migration of carriers and equilibrium is established.28,29

The free carrier depleted region width termed the depletion region width $W$ is equal to

\[ W = \left[ \frac{2\varepsilon k T}{q^2} \ln \left( \frac{N_A N_D}{n_i^2} \right) \left( \frac{1}{N_A} + \frac{1}{N_D} \right) \right]^{1/2} \]

Equation 14

Where $\varepsilon$, $q$, $n_i$, $N_A$, and $N_D$ are the permittivity, the elementary charge, the intrinsic carrier density, the acceptor density in the p-type material and the donor density in the n-type material, respectively. When the P-N junction is formed from the same material, the junction is termed homojunction (Figure 17); otherwise, P-N heterojunction is formed.29

It is worth noting that the depletion region is equally distributed on both sides of the junction in only one condition where both $N_A$ and $N_D$ are equivalent. In fact, the depletion region is wider in the lesser doped region.

![Figure 17 P-N junction at equilibrium and under illumination at short-circuit conditions; here carriers are generated from both sides of the interface. Reprinted with permission from Macmillan Publishers Ltd: Nature Photonics37 copyright 2009.](image-url)
3.2.2.2. CQD Depleted heterojunction

In theory, employing a P-N junction enhances the open circuit voltage as well as the potential for higher $J_{sc}$: with the quasi-neutral region extending from both sides of the junction the active material could double in thickness and hence allow doubling of the photons absorbed. Up to this point, a CQD homo-junction has not been yet reported due to the difficulty of controllably doping the CQD film; however, various CQD heterojunctions have been explored in recent years.\textsuperscript{24,44–49} In the early days of CQD photovoltaics, hybrid heterojunction devices employing PbS CQD and intrinsic organic layers were widely reported with sub-1% efficiencies.\textsuperscript{36,50,51} More recently in 2011, n-type Bi$_2$S$_3$ nanocrystals were employed in conjunction with an electron donor organic polymer but efficiencies recorded were sub-1% as well.\textsuperscript{44} The same research group also reported on fabricated a P-N heterojunction formed with n-type Bi$_2$S$_3$ nanocrystals and p-type PbS CQD, resulting in 1% efficiencies.\textsuperscript{45} The possible limitation of these structures can be summarized as follows:

1) Incompatibility of organic polymer and CQD material processing.

2) Employing intrinsic material in the hybrid heterojunction means almost no space charge region inside the CQD active material preventing efficient carrier collection.

3) The carrier mobility is a limited factor when employing Bi$_2$S$_3$ as well as its low doping concentration.

In 2010, Pattantyus-Abraham et al. reported a new architecture, termed the depleted heterojunction (DH), that successfully addressed the limitations of the Schottky junction as well as the limitations of the above mentioned CQD hybrid heterojunctions.\textsuperscript{24} The DH architecture employed an n-type wide bandgap transparent oxide electrode to extract electrons from the p-type CQD film. The charge separation here occurs efficiently at the front illuminated side of the cell: photogenerated electrons and holes are separated inside a depletion region formed at the n-p interface between n-type TiO$_2$ and p-type PbS. When suitably designed, the type-II heterojunction with TiO$_2$ provides a further driving force for electron transfer to the TiO$_2$ in view of the favorable conduction band offset and the holes are repelled into the p-type CQD film and collected by the barrierless ohmic contact (Figure 18). The enhancements inherent of the DH structure over previously reported architectures lead to an improved efficiency of over 5%.\textsuperscript{24}
Figure 18 Depleted heterojunction device schematic and band diagram under illumination. Electron injection is favored from the PbS CQD to the wide band gap oxide with the holes being repelled to the Au ohmic contact. Adapted with permission from Pattantyus-Abraham, A. G. et al. Copyright (2010) American Chemical Society.

The n-type electron acceptor electrode was further engineered to promote electron extraction without sacrificing the open circuit voltage circuit leading to a power conversion efficiency of 5.6%. Further studies employed ZnO in place of the TiO2 in a P-N depleted heterojunction with lead salt CQDs. The ohmic contact on the back side also plays an important role in the DH structure; specifically when larger bandgap CQD are employed, a deeper work function contact such as MoO3 improved the open circuit voltage of the device compared to just using Au contact. More recently, a record performance of 6% was achieved by optimizing the CQD film material properties; an atomic ligand strategy was pursued in place of employing organic ligands enabling enhanced electronic transport and successful surface passivation (Figure 19).

Figure 19 Organic and atomic ligands employed in CQD passivation strategies. Adapted by permission from Macmillan Publishers Ltd: Nature Materials copyright 2011.
In the DH structure, the minority carrier diffusion length limits the ability of going to thicker films necessary to enhance photon absorption. Analogous to the bulk heterojunction employed in organic photovoltaics, whereby an electron acceptor is blended with a donor forming a larger interfacial area throughout the active region,\textsuperscript{54–56} depleted bulk heterojunction CQD structure (DBH) leverages the use of highly nanoporous electron accepting electrode to enhance absorption in the CQD film leading to a power conversion efficiency of 5.5%. Across the near-infrared and the into the short-wavelength infrared, the DBH achieves vastly improved absorption resulting in an enhanced $J_{sc}$ (Figure 20).\textsuperscript{46}

![Image](image-url)

Figure 20 (a) Schematic of the DBH devices and SEM cross-section illustrating infiltrated PbS CQD in nanoporous TiO$_2$. (b) Absorption spectra comparison of DBH with DH structure and the expected spectral $J_{sc}$ showing 30% increase for the DBH architecture. Reprinted with permission from John Wiley & Sons, Inc. Advanced Materials\textsuperscript{46} copyright 2011.

### 3.2.3. Motivation for CQD Multijunctions

The capacity to tune the bandgap of colloidal quantum dots inherent of their quantum confinement has allowed the realization of optimal-bandgap single-junction solar cells.\textsuperscript{35,37} In principle this property also allows tandem and multijunction cells to be realized - devices that raise the ultimate limit on solar cell performance from 31% to 42% (tandem) and 49% (triple-junction).\textsuperscript{31,37}
In principle, PCE could be vastly increased if photons of different energies could be absorbed preferentially in cells of differing bandgaps. If the solar spectrum could be split between junctions of different bandgaps then (1) more of the solar radiation could be harnessed (2) each electron could be extracted with a potential closer to the incoming photon thus avoiding the loss of kinetic energy and most importantly (3) a higher power could be extracted from the same spectrum. Monolithically integrated multijunction structures are built by stacking different band gap junctions in optical series allowing the wider band gap materials to filter out the high energy photons leaving the less energetic one for the smaller bandgap materials (Figure 21a).26 Figure 21b depicts the maximum power efficiency that mutijunction solar devices can achieve with optimally chosen bandgaps.

![Diagram of multijunction solar cells](image)

Figure 21 (a) Triple bangap junction connected in electrical and optical series; The bottom cell absorbs the high energetic visible photons while the top cell absorbs the less energetic photons 31,37 (b)The maximum power conversion efficiency achievable by a single, two, three, four and infinite junctions under unconcentrated AM1.5 illumination. The optimal bandgap(s) for each case are indicated within the bars of the plot. Reprinted with permission from Macmillan Publishers Ltd: Nature Photonics37 copyright 2009.

One essential element in realizing multijunction solar cells is the ability of stacking the constituent junctions such that electron current from one cell recombines with the hole current from the adjacent cell. This is successfully achieved in epitaxial compound semiconductor devices using tunnel junctions 57–59 and in organic photovoltaics using recombination layers.60,61
In the tunnel junction (Figure 22a), degenerately-doped p++ and n++ materials produce an extremely thin junction in which the valence band on the p-side is energetically aligned with the n-side, and the depletion region is sufficiently thin that carriers can tunnel from one side to the other. Unfortunately, colloidal quantum dot solids, or materials of similar bandgap and compatible with CQD processing, are not available that achieve the sequential combination of p++ followed by n++ doping.

In organic photovoltaics (Figure 22b), suffering from lack of strong and controlled doping, a different approach is employed. In organic recombination layers, electron and hole currents from the electron transport layer (ETL) and hole transport layer (HTL) recombine at traps or metal nanoparticles inserted between these layers. Unfortunately, available HTL technologies such as (PEDOT:PSS) rely on aqueous and temperature (80-200°C) processing incompatible with high-performance CQDs.55,61
Figure 22 (a) The tunnel junction concept employed in epitaxial compound semiconductor devices. Degenerately-doped p++ and n++ materials produce an extremely thin junction in which the valence band on the p-side is energetically aligned with the n-side, and the depletion region is sufficiently thin that carriers can tunnel from one side to the other. (b) In organic recombination layers, electron and hole currents from the ETL and HTL recombine at traps or metal nanoparticles inserted between these layers.

In this work, we sought a new recombination strategy that would be compatible, in its materials processing, with CQDs; and that would enable the realization of a highly effective tandem solar cell. We also employ the quantum size-effect tuning to program the bandgaps of PbS CQD enabling spectrally selective solar harvesting resulting in the realization of the world’s first colloidal quantum dot tandem solar cell.21
3.3. Conclusions

This chapter provided the relevant concepts and literature review relating to CQD single junction solar cells. We first presented the attractive properties of colloidal quantum dots: they are solution-processed and allow easy access to the entire solar spectrum.

We established that colloidal quantum photovoltaics has vastly evolved since its first report in 2005\textsuperscript{36} and the reported efficiencies have increased at a remarkable fast pace reaching 6\% in 2011.\textsuperscript{19} In the early years, Schottky junctions were extensively adopted. Their main limitations are: (1) the pinning of the Fermi energy level at the interface thus limited the value of the $V_{oc}$, (2) the inability of the photogenerated minority carriers to traverse long transport lengths without succumbing to recombination processes thus limiting the active material thickness.

In 2010, the depleted heterojunction structure was conceptualized to address the limitations of the Schottky junction and resulted in the best efficiencies to date; a p-type PbS film is brought into contact with an electron accepting wide band gap n-type oxide promoting efficient electron extraction.

We concluded by briefly presenting the motivation behind the novel research work of this thesis based on the fabrication of the world’s first tandem colloidal quantum dot solar cell. The details of this work are presented in chapters 5, 6 and 7. We describe in chapter 4 the material and device processing methodology followed by the various characterization techniques employed in this thesis.
Chapter 4 Experimental Methodology

We discussed the relevant theoretical concepts and published reports regarding CQD photovoltaics in chapters 2 and 3 and introduced the motivation behind our work. In this chapter, we layout the experimental details of how PbS CQD are processed in solution and solid-state to fabricate single and tandem junction devices. We also describe the various material and device characterization techniques employed in this work.

4.1. PbS CQD solution processing

In this dissertation, we employ different sizes of PbS quantum dots corresponding to 1.6 eV, 1.3, 1.1 and 1 eV junctions. We describe the solution processing of the different size of PbS CQD in the subsequent sections (Figure 23). All chemicals were used as received unless stated otherwise.

Figure 23 Diagram illustrating the sequence followed for PbS CQD solution processing leading up to device fabrication.
4.1.1. Visible 1.6 eV PbS CQD Synthesis and Purification

Bis(trimethylsilyl)sulphide \((\text{C}_6\text{H}_{18}\text{S}_2\text{Si;TMS})\) (0.18 g, 1 mmol) was added to 1-octadecene (ODE) (10 mL), which had been dried and degassed by heating to 80°C under a vacuum for 24 hours. A mixture of oleic acid (1.34 g, 4.8 mmol), oleylamine (0.134 g, 1.5 mmol), PbO (0.45 g, 2.0 mmol), and ODE (14.2 g, 56.2 mmol) was heated to 95°C under vacuum for 16 hours then placed under Ar. The flask temperature was increased to 120°C and the TMS/ODE mixture was injected. After injection, the temperature dropped to ~95°C, and the flask was allowed to cool gradually to 36°C. The nanocrystals were precipitated with 50 mL of distilled acetone and centrifuged. After discarding the supernatant, the precipitate was redispersed in toluene. The nanocrystals were precipitated again with 20 mL of acetone, centrifuged for 5 min, dried, and finally dispersed in toluene (~350 mg/mL). PbS nanocrystals were then refluxed with toluene at 90°C. The nanocrystals were precipitated two more times with acetone, and finally redispersed in octane at a concentration of 25 mg/mL. The above synthesis was performed by Dr. Larissa Levina. Figure 24 illustrates PbS nanocrystals after synthesis.

Figure 24 Transmission electron microscopy of PbS nanocrystals.

4.1.2. Infrared 1 eV PbS CQD Synthesis

Infrared PbS CQD (1.3, 1.1 and 1 eV) employed in this thesis were synthesized using a variation of the widely employed synthesis reported in literature. In particular, the 1 eV PbS CQD were synthesized following this procedure: TMS (0.18 g, 1 mmol) was added to ODE (10 mL), which had been dried and degassed by heating to 80°C under vacuum for 24 hours. A mixture of PbO (0.90 g, 4.0 mmol), and oleic acid (17.82 g, 63.2 mmol) was heated to 110°C under vacuum for
16 hours then placed under Ar. The flask temperature was increased to 110°C and the TMS/ODE mixture was injected. After injection, the temperature dropped to ~95°C, and the flask was allowed to cool slowly to 36°C. The nanocrystals were precipitated by adding 10 mL of anhydrous methanol and were centrifuged under ambient conditions. After discarding the supernatant, the precipitate was redispersed in toluene. The nanocrystals were re-precipitated again using 3.0 mL of methanol, centrifuged for 5 min, dried, and finally dispersed in toluene (~200 mg/mL). The above synthesis steps were performed by Dr. Larissa Levina.

4.1.3. Infrared 1 eV PbS CQD Solvent Change

Further methanol washing was conducted in a nitrogen filled glovebox to minimize the oleic acid ligands at the surface of the quantum dots, enabling efficient solid-state cross linking. The solution received after synthesis was split into two test tubes of equal amount. 12 mL of methanol was added to each test tube and centrifuged for 5 min. The resulting clear supernatant was discarded and the remaining sediments were vacuum dried for 10 min. 2 mL of toluene was then added to each test tube and the nanocrystals were carefully redispersed. The methanol washing was then repeated with the vacuum drying lasting 30-60 min at this stage. The CQD were finally redispersed in octane at a concentration of 37 mg/mL.

4.2. PbS CQD Device Fabrication

The solutions of PbS CQD are deposited via layer-by-layer spin-coating process. Details of the device fabrication processes are detailed below.

4.2.1. Substrate Cleaning Procedure

Commercial ITO substrates (Delta Technologies, 100 Ω/□, 1 in. by 1 in. squares) were cleaned prior to CQD film deposition in a sequence of multiple 30 min sonifications: first, in 1% by volume of Triton X-100 aqueous solution, rinsed with abundant deionized (DI) water to remove any bubbles, second, in isopropyl alcohol, and finally in deionized water. The substrates were then dried by N₂ flow.
4.2.2. High Temperature Nanoparticle TiO$_2$ Electrode Preparation

TiO$_2$ nanoparticles with 10-30 nm diameter originally dispersed in terpineol (DSL90-T, Dyesol) were further diluted in terpineol and spin-coated onto the ITO substrates. The nanoparticles were diluted with terpineol (1:3 by weight), spin-cast at 1500 rpm, and placed on a hot plate preheated to 120°C. Substrates were then heated at 200°C for 15 min and 400°C for 60 min. Subsequently, the TiO$_2$ substrates underwent TiCl$_4$ treatment in a 60 mM solution in DI water at 70°C for 30 min. The substrates were finally rinsed with DI water, and heated at 400°C for 60 min. The electrode processing was carried out in a fumehood in ambient conditions.

These electrodes were employed as the electron acceptor in the visible 1.6 eV PbS CQD solar cells.

4.2.3. Room-Temperature Electrode Preparation

Room-temperature processed electrodes are essential in our work. Here we describe the fabrication process of all room-temperature sputtered n-type oxides used as electron accepting electrodes for the infrared junction and those used as part of the graded recombination layer of our tandem junctions (refer to chapter 6 for further details).

ITO, AZO and TiO$_2$ (all from Kurt J. Lesker) were deposited by an RC magnetron sputtering (Angstrom Engineering Åmod deposition) system in a glovebox (Innovative Technology) at room temperature. The 50 nm ITO was sputtered in 1% O$_2$/Ar environment at a pressure of 5 mtorr and a rate of 0.25 Å s$^{-1}$, the 50 nm AZO in pure Ar or 1% O$_2$/Ar at 5 mtorr at a rate of 0.25 Å s$^{-1}$, and the 40-50 nm TiO$_2$ under pure Ar or 1-3% O$_2$/Ar at 5 mtorr at a rate of 0.20 Å s$^{-1}$. A thermometer monitoring substrate temperature indicated processing temperatures no higher than 30°C.

4.2.4. Film Deposition

PbS CQDs (1.6 eV) at a concentration of 25 mg/mL in octane were deposited in a layer-by-layer fashion. Two drops of CQDs were dispensed onto the substrates through a 0.2 µm filter and spin-cast at 2,500 r.p.m. for 10 sec; five drops of a 0.2% mercaptopropionic acid (MPA) in methanol solution were applied to the CQD film through a 0.2 µm filter for 3 sec then spin-cast at 2,500
Finally, three rinse steps were carried out, first with methanol, then with acetone, and finally with octane, each followed by spinning the substrate at 2,500 r.p.m. for 10 sec. This procedure was repeated until the desired film thickness (~200 nm) was reached (12 layers). The device was post-soaked in 10% MPA in methanol for 30 min, and then rinsed with methanol, acetone and octane. Employing >0.2 MPA/methanol solution during the layer-by-layer deposition led to higher rough film surface resulting in complete shorting in devices.

PbS CQDs (1 eV) at 37.5 mg/mL in octane were deposited on the substrates using the same method to achieve a 300-nm-thick film (10 layers). A 10–30% MPA/methanol solution was used for the solid-state treatment, and no post-soaking step was carried out. Employing < 10% MPA/methanol solution with 1 eV PbS CQD led to highly resistive films.

4.2.4.1. Special Considerations for Tandem Junction Fabrication

In order to fabricate our monolithically integrated tandem structure, we needed to deposit multiple layers of small bandgap quantum dots on top of multiple layers of large bandgap quantum dots and around 170 nm thick of sputtered n-type oxides (refer to structural details in chapter 6). The MPA treatment concentration, spinning speed as well as the spinning environment conditions needed to be optimized to obtain final smooth films necessary for efficient solar cells. We increased the spinning time of each step to 20 sec to allow films to spread slowly and added a drying step employing a nitrogen gun after each layer spun. Figure 25 compares our first generation tandem solar cells surface full of pinholes with our much improved efficient devices having near-perfect morphology.
4.2.5. Metallization

For the top contact, MoO$_3$ was used as Au replacement; with its deep work function, it resulted in improved open circuit voltages. 10-15 nm of MoO$_3$ (Alfa Aesar) was deposited by thermal evaporation at a rate of 0.4 Å/s and 150 nm of Ag (Lesker) was deposited by thermal evaporation at a rate of 1 Å/s. Both elements were deposited under 5 x 10$^{-7}$ Torr chamber pressure. A shadow mask with a 4×4 array of 2.7 mm diameter circular contacts was used to define the contact area.

4.3. Characterization Techniques

Herein, we describe both material and device characterization techniques employed in our study.

4.3.1. Material Characterization

4.3.1.1. Absorption

Optical absorption measurements were carried out using a Varian Cary 500 UV-Vis-IR Scan spectrophotometer with an attached integrating sphere. For the PbS CQD absorption characterization, devices were measured without their top reflective metal contact. Single-pass absorption through the film was obtained with a bare bottom electrode taken as a reference. For the characterization of the n-type oxides, each material was deposited onto a transparent glass
substrate. The same thickness of 50 nm was used for each of the following three samples; MoO₃, AZO and TiO₂. The absorption spectra of all materials and their interpretations are presented in Appendix 1.

4.3.1.2. Scanning Electron Microscopy (SEM)

SEM was employed to image the PbS CQD films in the tandem structure. SEM was performed on a Hitachi S-4700 at 3 kV. For TEM analysis, ~ 50 nm thick cross sectional regions were prepared using focus ion beam (FIB). Each specimen’s surface was coated with carbon, e-beam and ion beam platinum prior to sample preparation for protection.

4.3.1.3. Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS)

UPS allows determination of the absolute value of work function (Fermi level, $E_f$) and ionization potential (equivalent to valence band edge, $E_v$) of semiconductor materials. Ultraviolet light, with energy lower than 100 eV, irradiates the surface of the sample and valence electrons are extracted. The kinetic energy of the emitted electrons is analyzed. UPS was carried out using He I (21.22 eV) photon lines from a discharge lamp. The n-type oxides were deposited on a commercial ITO substrate. The thickness of MoO₃, AZO and TiO₂ were all 50 nm in order to eliminate background signal from the ITO substrate. The full UPS spectra for MoO₃, AZO and TiO₂ and their interpretation are shown in Appendix 2. Special care was taken to avoid air exposure of the samples during transfer from the deposition chamber located in the glovebox to the XPS facility.

XPS is a quantitative spectroscopic technique to ascertain the elemental composition and chemical state of thin films. Here, X-rays hit the sample surface and the binding energy of the emitted electrons is measured. The full details of the measurements done and their interpretation are presented in Appendix 2.

4.3.1.4. Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is a type of potentiodynamic electrochemical measurement. It has been applied to obtain the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) levels of organic materials and quantum dots, as well as the electron affinity of semiconductors. Here we use it to measure the electron affinity (equivalent
to conduction band edge $E_c$) of PbS CQD and n-type oxide materials. The results are shown in Appendix 3. We use the Ag/AgNO$_3$ (0.01M acetonitrile) reference electrode in the measurement, which has the absolute value of -4.7 eV.

**4.3.1.5. Field Effect Transistors (FET)**

We built FET test structures with the goal of estimating the order of magnitude of the free carrier densities within each oxide layer. We use a similar method to that described in the reference 54 to fabricate FET devices. Our FET devices showed good modulation with applied gate bias (drain current $I_d$ vs gate bias $V_g$).

We calculated the majority carrier mobility from the measured transconductance

$$g_m = \left. \frac{\partial I_d}{\partial V_g} \right|_{V_g \text{ const}} = \frac{W C_i V_d}{L} \mu$$

**Equation 15**

by taking the slope of the $I_d$ vs. $V_g$ curve in the linear regime at a constant $V_d$. The channel length $L$ was equal to 2.5 μm, while the channel width $W$ was equal to 2 mm; the capacitance per unit area of the insulating layer was $C_i = 100 \ \mu$F/cm$^2$. The conductivity ($\sigma$) is determined from the slope of $I_d$ vs $V_d$ at zero gate bias. The doping density of the specimen is then calculated with the following equation

$$\sigma = q \mu n$$

**Equation 16**

where q is the electronic charge, and n is the electron doping density.

During our measurements, we saw appreciable hysteresis that rendered our mobility measurements – and therefore our extracted free carrier densities – accurate to within somewhat better than one order of magnitude. For the purpose of this work, that degree of accuracy is sufficient (e.g. providing reasonable accuracy translating into the spatial band diagrams of the materials, and supporting the assertion that MoO$_3$ and AZO are both essentially degenerately-doped while TiO$_2$ is much lower doped). Further measurement details are in Appendix 4.
4.3.2. Device Characterization

4.3.2.1. J-V Characteristics

All solar cells in this work were measured in an inert N$_2$ environment. The current–voltage characteristics of the CQD solar cells were recorded using a source meter (Keithley). AM1.5 illumination was accomplished using a solar simulator (Science Tech). The solar spectrum at AM1.5 was simulated to within Class A specifications (less than 25% spectral mismatch) with a Xe lamp and filters (Solar Light Company Inc.) with measured intensity at 100 mW/cm$^2$. The illumination area was apertured to 0.049 cm$^2$ using two collimated apertures, one in the optical pathway and the other immediately before light impinging on the device under test. The source intensity was measured with a Melles-Griot broadband power meter (responsive from 300 to 2000 nm). The accuracy of the power measurement was estimated to be 5%. The tandem CQD solar cell had a GRL area of 0.18 cm$^2$ and a top contact area of 0.06 cm$^2$. The aperture is smaller than the contact size to ensure that there is no lateral current collection. This is done to minimize any device-size effects. An absolute current of 0.5 mA corresponds to 10 mA cm$^2$ when an illumination area of 0.049 cm$^2$ is used to calculate the current density.

4.3.2.2. Spectral EQE

The external quantum efficiency spectrum was acquired by passing the output of a 400 W Xe lamp through a monochromator and using appropriate order-sorting filters. The resultant monochromatic beam also passed through an optical chopper operating at a frequency of 100 Hz coupled to the input of a Stanford Research Systems lock-in amplifier. The collimated output of the monochromator was measured through a 0.0079 cm$^2$ aperture with calibrated Newport 818-UV and Newport 818-IR power meters as needed. The measurement step was 20 nm and the intensity varied with the spectrum of the Xe lamp. The monochromatic light was coaligned with an AM 1.5 source (Newport Corporation) providing one-sun intensity of continuous white light bias. The photogenerated current was then measured using a lock-in amplifier.

4.4. Summary

In this chapter, we described the experimental methodology employed to process the solution-processed PbS CQD, to deposit thin films onto substrates and to fabricate single junctions as well as tandem structures. We also described all the characterization techniques employed to provide
further insights regarding the various materials we used in this work as well as device properties. The details of each characterization technique are presented in Appendix 1 through 4.
Chapter 5 Constituent Junctions of CQD Tandem Solar Cell

We established in chapter 3 that colloidal quantum dots enable multijunction solar cells using a single material, PbS CQD, tunable using the quantum size effect. In this chapter, we report the systematic engineering of the 1.6 eV visible junction,\textsuperscript{53} optimal as the front cell responsible for visible wavelength harvesting, and the infrared junction harnessing the lower energy photons\textsuperscript{66} both of which are the constituent junctions of CQD tandem solar cells.\textsuperscript{21} We also note that depleted heterojunction colloidal quantum dot photovoltaics\textsuperscript{24} have, to date, shown the highest CQD PV device efficiencies and thus we employ this architecture in this work to fabricate efficient visible and infrared single junction devices. We rationally optimize each of the device’s collecting electrodes—specifically the heterointerface with the electron accepting electrode for maximum efficiency. The work on the visible junction was done in close collaboration with Dr. Xihua Wang.

5.1. 1.6 eV PbS CQD Visible Junction\textsuperscript{53}

Quantum confinement dominates the exciton energy in 1.6 eV CQD PbS films: this bandgap is fully four times that of the underlying bulk semiconductor bandgap of 0.4 eV. While this dramatic bandgap-tuning is readily achieved at the time of synthesis, it demands, within the photovoltaic device, significant reengineering of the carrier-collecting electrodes to match the altered LUMO and HOMO levels of the light-absorbing quantum dot films. The absorption spectrum of the visible PbS CQDs employed herein is shown in Figure 26a. The exciton peak at 766 nm indicates a bandgap of \(~1.6\) eV. In light of the considerably shallower electron affinity in 1.6 eV PbS CQD films relative to all prior reports (1.3 eV and smaller bandgaps), we first experimentally measured the bandedge of the films, and of various electrodes, using cyclic voltammetry (Figure 26 b and c). The HOMO level was \(~5.2 \pm 0.1\) eV for the quantum dot film, from which we estimate the LUMO level to be at \(~3.6 \pm 0.1\) eV. To favor electron injection from the quantum dot film into electron-accepting TiO\textsubscript{2}, the electron affinity of TiO\textsubscript{2} should be deeper than the LUMO level of the quantum dot film. Cyclic voltammetry applied to our TiO\textsubscript{2} electrode indicated an electron affinity of \(~3.8 \pm 0.1\) eV (Figure 26c). We thus estimated a 0.2 eV energy difference in band offset favoring electron injection into the TiO\textsubscript{2}. In view of the small (sub 50 meV) exciton binding energy in PbS CQDs, this provided a more than adequate driving force at the heterointerface. Any deeper TiO\textsubscript{2} bandedge—such as the \(-4.0\) eV electron affinity reported in
sputtered$^{21}$ TiO$_2$—would continue to favor electron extraction, but could unduly compromise open-circuit voltage $V_{oc}$ (Table 2). In general, the lesser of the Femi level difference between electron-collecting and hole-collecting electrodes, and the quasi-Fermi level splitting inside the PbS film, sets the upper limit of open-circuit voltage $V_{oc}$ in heterojunction solar cells. In this work, using nanoparticle TiO$_2$, with its -3.8 eV electron affinity, led to a superior $V_{oc}$ of 0.7 V (Table 1) and 3% solar power conversion efficiency.

Figure 26 Engineering of electron-accepting materials and hole-collecting top-electrodes. (a) Absorption spectrum of 1.6 eV PbS CQD. (b) Cyclic voltammetry results of PbS CQD film. (c) Cyclic voltammetry results of various electron-collecting TiO$_2$ films. (d) Schematic of energy band diagram at PbS/top-electrode interface. The PbS/Au contact shows an unfavored band bending of collecting holes. The PbS/MoO$_3$ contact shows an enhanced band bending via surface-field effect. Reprinted with permission from Applied Materials$^{53}$ Copyright 2011 American Chemical Society.
When working with larger-bandgap materials, challenges arise in constructing barrier-free ohmic contacts using noble metals. We show that this problem may be solved by using an ultra-deep-work function transparent conductive oxide. We employed MoO$_3$, a heavily doped deep-work-function metal oxide, to achieve ohmic contact to 1.6 eV PbS CQD film. The thermally evaporated MoO$_3$ was characterized$^{23}$ and had a work function of 5.4 eV, and provided direct work-function match to the HOMO level (5.2 eV) of 1.6 eV PbS CQD film. Slight band-bending at PbS/MoO$_3$ interface in fact favors hole collection and achieves a mild back surface field that repels electrons from this interface (Figure 26d).$^{67}$ We showed the enhanced PV device performance with MoO$_3$ top electrode compared to the commonly employed Au top electrode (Au work function 5.1 eV). Attractively, evaporated Ag serve as a highly effective reflective top electrode atop MoO$_3$, obviating the use of Au entirely.

We conclude this section with more complete characterization of our PV devices behaviors. In Figure 27, we provide current density-voltage (J-V) and external quantum efficiency spectra for the best PV device achieved through the combination of these optimization strategies reported above.

<table>
<thead>
<tr>
<th>TiO$_2$ type</th>
<th>PbS CQD bandgap (eV)</th>
<th>top-electrode</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanoparticle</td>
<td>1.6 eV</td>
<td>MoO$_3$</td>
<td>0.70 ± 0.2</td>
<td>9.5 ± 0.5</td>
<td>49 ± 3</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>sputtered</td>
<td>1.6 eV</td>
<td>MoO$_3$</td>
<td>0.61 ± 0.1</td>
<td>8.9 ± 0.2</td>
<td>50 ± 2</td>
<td>2.7 ± 0.2</td>
</tr>
<tr>
<td>nanoparticle</td>
<td>1.6 eV</td>
<td>Au</td>
<td>0.64 ± 0.1</td>
<td>8.1 ± 0.4</td>
<td>49 ± 2</td>
<td>2.6 ± 0.2</td>
</tr>
</tbody>
</table>
Characterization of PbS CQD based solar cells. (a) AM1.5 J-V characteristics. \( V_{oc} = 0.70 \) V, short-circuit current \( J_{sc} = 10 \) mA/cm², FF = 50%, PCE = 3.5%; (b) EQE spectrum of the device. Reprinted with permission from Applied Materials© Copyright 2011 American Chemical Society.

In summary, we synthesized visible quantum dots (1.6 eV PbS CQD) and applied them to photovoltaic devices with electron accepting TiO₂ and hole-collecting MoO₃. We characterized and further customized the electrical properties of the carrier-collecting electrodes. PV devices with an enhanced \( V_{oc} \) of 0.70 V are only obtained after engineer carrier-collecting electrodes for both electrons and holes. The 3.5% AM1.5 PCE achieved herein represents the highest power conversion efficiency reported in a visible (~1.6 eV bandgap) quantum dot PV device. We now transition to the development of the 1 eV infrared single junction.

### 5.2. 1 eV PbS Infrared CQD Junction

Colloidal quantum dots enable solution-processed photovoltaics capable of harvesting the full spectrum of the sun’s power including the half that resides in the infrared. Unfortunately, the highest-performing colloidal quantum dot photovoltaics reported to date have relied on annealing TiO₂ electrodes at temperatures of 500°C or greater. High-temperature fabrication steps add to manufacturing cost and energy payback time. Steps requiring temperature treatments greater than 200°C generally rule out the use of transparent flexible substrates desired for conformable photovoltaics. Furthermore, the fabrication of multijunction photovoltaic devices based on solution-processed materials necessitates low-temperature processing of the back cell(s) for thermal compatibility with prior layers. In this section we report an electrode strategy that enables a depleted heterojunction CQD PV device to be fabricated entirely at room temperature.
5.2.1. TiO$_2$/PbS CQD Heterojunction Devices Based on Room-Temperature Oxide Deposition

We first attempted building electrodes at room temperature by sputtering 100 nm of TiO$_2$ under various Ar and O$_2$ concentrations onto ITO-coated glass substrates. Characterization of the materials (Appendix 2-Figure SI 5, Appendix 3-Figure SI 11, Appendix 4-Figure SI13) indicated that the conduction band edge of these electrodes could be tuned through sputter conditions. A higher O$_2$ concentration led to a deeper electron affinity and lower doping with tuning possible from ~4.0 eV down to ~4.2 eV.

From considerations of electron affinity depicted in Figure 28 and summarized in Table 3, we expected that these electrodes should form viable charge-separating heterojunctions when coupled to 1.3 eV-bandgap colloidal quantum dots ($\chi = -3.8$ eV$^{24,47}$). Using the same analysis, we anticipated that only the deeper-work function electrodes would form charge-separating junctions with 1.0 eV bandgap colloidal quantum dots ($\chi = -4.0$ eV$^{21,47}$) of interest in small bandgap devices. These expectations were confirmed for the case of the high temperature-processed nanocrystalline TiO$_2$ paired with the 1.0 eV bandgap quantum dots. With its shallow electron affinity (~3.8 eV$^{53,74}$), the electrode forms an unfavorable band offset with the 1.0 eV bandgap quantum dot film. Consistent with our expectations, poor performance is observed in these devices (Figure 28b). To further verify this picture, we investigated the dark characteristics of our devices under forward bias (Figure 28c). At high forward bias, the device shows higher majority carrier injection and 2 orders of magnitude higher current densities than the devices on the resistive sputtered electrodes. This result provides a further impetus for new electrodes suitable for photovoltaics involving small-bandgap 1.0 eV quantum dot films, the back cell in tandem colloidal quantum dot photovoltaics.$^{21}$
Figure 28 (a) Energy level diagram showing the HOMO and LUMO energies of 1 eV PbS quantum dots and the band edges of the isolated TiO$_2$ and AZO materials with the acronyms used in this work explicitly stated.
(b) J-V characteristics of 1 eV CQD devices on various stand-alone TiO$_2$ (solid lines, DS90 vs 100 nm of S-TiO$_2$ and M-TiO$_2$) and of 1.3 eV CQD on stand-alone TiO$_2$ (dashed lines, 100 nm of S-TiO$_2$, and M-TiO$_2$) under AM1.5 illumination. The series resistance in the sputtered TiO$_2$ is in the range of 10-40 kΩ. (c) Dark J-V of 1 eV CQD devices made on DS90 vs 100 nm of S-TiO$_2$ and M-TiO$_2$. Reprinted with permission from Nano Letters$^{66}$ Copyright 2011 American Chemical Society.

Table 4 Properties of electron-accepting materials.$^a$ Adapted with permission from Nano Letters$^{66}$ Copyright 2011 American Chemical Society.

<table>
<thead>
<tr>
<th>Material</th>
<th>Acronym</th>
<th>Electron mobility (cm$^2$/V s)</th>
<th>Doping (cm$^{-3}$)</th>
<th>Electron affinity, $\chi$ (eV)</th>
<th>Work function, $\phi$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ sputtered in Ar — shallow electron affinity</td>
<td>S-TiO$_2$</td>
<td>$\sim 3 \times 10^{-5}$</td>
<td>$\sim 7 \times 10^{15}$</td>
<td>4.0</td>
<td>4.1</td>
</tr>
<tr>
<td>TiO$_2$ sputtered in 1% O$_2$/Ar — medium electron affinity</td>
<td>M-TiO$_2$</td>
<td>$\sim 2 \times 10^{-5}$</td>
<td>$\sim 3 \times 10^{15}$</td>
<td>4.1</td>
<td>4.2</td>
</tr>
<tr>
<td>TiO$_2$ sputtered in 3% O$_2$/Ar — deep electron affinity</td>
<td>D-TiO$_2$</td>
<td>$\sim 1.6 \times 10^{-5}$</td>
<td>$\sim 1.5 \times 10^{15}$</td>
<td>4.2</td>
<td>4.45</td>
</tr>
<tr>
<td>AZO sputtered in Ar — shallow work function</td>
<td>S-AZO</td>
<td>$&gt; 5 \times 10^{20}$</td>
<td>$&gt; 4.1^b$</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>AZO sputtered in 1% O$_2$/Ar — medium work function</td>
<td>M-AZO</td>
<td>$10^{-2}$</td>
<td>$5 \times 10^{19}$</td>
<td>4.1</td>
<td>4.1</td>
</tr>
</tbody>
</table>

$^a$ The increase in O$_2$/Ar content deepens the electron affinity of the TiO$_2$ electrode$^{73,75}$ and the work function of the AZO. b AZO in pure Argon is expected to have a higher doping and higher electron affinity than AZO in oxygen content reported in Ref 12; The change in electron affinity with the inclusion of oxygen during oxide sputtering is reported in refs 66 and 68.

In light of the above band-edge considerations, more surprising was the fact that all other devices showed poor performance compared to high-temperature-processed nanocrystalline TiO$_2$ controls. Especially problematic was the very large series resistance of all devices based on sputtered electrodes. This led to very poor fill factor (see Figure 28b). The electron mobility inside the sputtered oxide films$^{21}$ was found to be low ($1 \times 10^{-5}$ cm$^2$/V s; Appendix 4-Figure SI 13); using a simple model (Appendix 5-Figure SI 14)$^{76}$ we confirmed that a 100 nm thick layer of this material could indeed account for the observed poor performance.

We moved to much thinner coatings of the electron-accepting oxide to overcome low mobility. A 30 nm thick TiO$_2$ layer, the thinnest compatible with complete coverage of the underlying electrode using RF sputtering, and the thinnest leading to a rectifying junction, produced an improvement over the 100 nm titania layer depicted in Figure 29a but provided a still unacceptable fill factor and overall performance. Our models suggested that from a mobility standpoint 30 nm should have been sufficiently thin to reduce the series resistance of this layer to an insignificant level (Appendix 5- Figure SI 14). However, further examination of model results revealed that when the n-type titania thickness was reduced to the point that the electron acceptor would now be fully depleted under normal photovoltaic operation, the work function in the bottom ITO electrode now began to limit the open-circuit voltage of our device (Appendix 5-Figure SI 14), degrading performance unacceptably through this new mechanism.
A shallow-work-function, heavily doped electrode such as aluminum-doped zinc oxide (AZO) compatible with room-temperature sputtering should in principle resolve the preceding compromise. However, we observed negligible photovoltaic performance from all devices on the highly doped electrode AZO (Figure 29b). We interpreted the poor photovoltaic response as unfavorable interfacial junction and incompatibility of these two materials; it has been previously reported that ZnO surfaces are prone to significant chemical change in the presence of thiols. Additionally, pinning of the HOMO level of PbS CQDs has been reported at the interface with the ZnO.\textsuperscript{77} These mechanisms are consistent with our observation of a low open-circuit voltage.

![Figure 29 J-V characteristics of 1 eV CQD devices on thin (30 nm) (a) S-TiO\textsubscript{2} and M-TiO\textsubscript{2}. The series resistance drops to 800 ohm but is still significant. (b) S-AZO and M-AZO. Using AZO without TiO\textsubscript{2} leads to](image-url)
5.2.2. The Donor-Supply Electrode Concept

The combined failure of thick sputtered TiO$_2$ due to high resistance, of thin TiO$_2$ due to its insufficiently shallow work function, and of AZO due to materials incompatibility together led us to consider a new design for a multilayer electrode. Combining these insights into a new electrode strategy, we took the view that immediately adjacent to the CQD layer there should be an electron acceptor having the desired electron affinity and proven chemical compatibility with the quantum dot film. Such materials are available via low-temperature sputtering as noted above (Table 3). Contacting the electron acceptor using a heavily doped, shallow work function electrode would enforce a large built-in voltage in the overall device. Desirably, if its work function was shallower than that of the electron acceptor, this conductive electrode would increase the free-carrier density in the electron acceptor via charge-transfer doping. This would offer an added benefit: it would overcome the low mobility of the room-temperature-sputtered electron acceptor by increasing its conductivity via the achievement of a high free carrier density (Appendix 5- Figure SI 15).

We termed this strategy the “donor-supply electrode”, or DSE and depict it in Figure 30a. We fabricated colloidal quantum dot devices atop DSEs built via all-room-temperature-sputtered AZO and TiO$_2$ with the latter being the topmost layer of the DSE.
Figure 30 (a) Schematic illustrating the DSE concept: We present the 1 eV CQD device structure with an emphasis on the two-diode model of the heterojunction formed between PbS and TiO₂ before and after the application of DSE. We show that with a stand-alone TiO₂ electrode the equivalent series resistance is mainly restricted to the electrode resistance (>10 kΩ from Figure 28); the deep work function in the bottom ITO...
limits the performance of the device. When DSE is integrated into the device, the electrons are transferred from the now shallow work function highly doped AZO to the TiO$_2$. The equivalent resistance is reduced significantly. (b) Band diagram showing the relative band alignment of the AZO/TiO$_2$ ($\Delta\phi_1$) and the barrier height between TiO$_2$ and PbS CQD ($\Delta\phi_2$). Reprinted with permission from Nano Letters$^{66}$ Copyright 2011 American Chemical Society.

The light and dark J-V characteristics are shown in Figure 31. The optimal DSE device achieved a short-circuit current of 17.4 mA/cm$^2$, an open circuit voltage of 0.4 V, and a fill factor of 58%$^{39,47,70}$ (the latter achieved via low series resistance (110 ohms) and high shunt resistance (14 kΩ)). The result was a 4% power conversion efficiency under AM1.5 100 mW/cm$^2$ illumination, a record for a 1 eV bandgap CQD PV device.

Figure 31 J-V characteristics of 1 eV CQD devices on M-AZO followed by (blue) S-TiO$_2$ (red) M-TiO$_2$ and (green) D-TiO$_2$; M-TiO$_2$ is the optimal DSE with power conversion efficiency of 4%, and FF of 58% under
AM1.5 illumination (a) and in the dark (b). Reprinted with permission from Nano Letters\textsuperscript{66} Copyright 2011 American Chemical Society.

We now discuss in further detail the design requirements for a DSE optimally matched to the requirements of CQD photovoltaics. The charge-transfer doping concept has been employed to beneficial effect, though with a different goal, in high-electron-mobility transistors (HEMT).\textsuperscript{78,79} HEMTs employ a heterojunction between a highly doped n-type material and a not-intentionally doped channel layer. The lack of dopant ions incorporated into the channel is conducive to high mobility, and charge-transfer from the adjacent highly n-doped layer enables control over threshold voltage. Our DSE uses the charge-transfer doping concept for a distinct purpose. It fulfills simultaneously the requirements of

(1) room-temperature processing;

(2) carefully chosen bandedge for high $J_{sc}$ without compromise to $V_{oc}$;

(3) highly doped and conductive under-layer to generate an equivalent highly doped electrode.

We identify two key factors influencing the performance of our DSE-based devices (Figure 30b): the band alignment of the AZO/TiO$_2$ interface ($\Delta \phi_1$), and the barrier height between TiO$_2$ and PbS CQD ($\Delta \phi_2$).

5.2.3. Optimal Design of the DSE for CQD Photovoltaics

DSE charge transfer depends heavily on the band alignment of the highly doped donor layer (AZO) relative to the resistive low doped charge-accepting layer (TiO$_2$). In our architecture, we expect the devices where the work function of the AZO is shallower than that of the TiO$_2$ to inject electrons. We employed M-AZO ($\varphi = -4.1$ eV) as the underlayer and fabricated 1 eV PbS CQD devices with electron acceptors having three different work functions: S-TiO$_2$ ($\varphi = -4.1$ eV), M-TiO$_2$ ($\varphi = -4.2$ eV), and D-TiO$_2$ ($\varphi = -4.45$ eV). The best results were achieved when M-AZO ($\varphi = -4.1$ eV) was combined with M-TiO$_2$ ($\varphi = -4.2$ eV). Here, proximity of the TiO$_2$ to the AZO resulted in charge-transfer and an increase in carrier density in the TiO$_2$. When S-TiO$_2$ was employed, charge-transfer was not favored, and a poor (S-shaped) $J$-$V$ near open-circuit conditions was observed experimentally (Figure 31) and predicted in the model (Figure 32). This
is reinforced by the low forward-biased dark current for this device, also seen both in experiment and model, explained by the resistance of the undoped TiO$_2$. When D-TiO$_2$ is employed, band-bending becomes unfavorable in the colloidal quantum dot film from the point of view of electron extraction into the TiO$_2$, also resulting in a poor J-V near $V_{oc}$ seen both in experiment and theory. Observed and modeled high forward dark current confirms that charge-transfer doping was successful, and thus that the failure is instead of the barrier in the CQD film at $V_{oc}$ conditions.

Figure 32 Band diagram near $V_{oc}$ of 1 eV CQD devices made on M-AZO followed by S-TiO$_2$, M-TiO$_2$ and D-TiO$_2$ is depicted with their simulated J-V characteristics in the light (a) and in the dark (b). The simulated curves are in agreement with the experimental behavior of the corresponding devices. SCAPS was used for modeling (Appendix 5). Reprinted with permission from Nano Letters$^{66}$ Copyright 2011 American Chemical Society.
In Figure 33 we use quantum dot size-effect tuning to vary the band offset between the colloidal quantum dot film and the electron-accepting TiO$_2$. When larger-bandgap (1.3 eV) quantum dots are employed, the choice of electron acceptor between M-TiO$_2$ or S-TiO$_2$ has only a small influence on device response: the main effect is a slight decrease in open-circuit voltage for the M-TiO$_2$ relative to the S-TiO$_2$ case due to a sacrifice of slightly more photoelectron energy at the heterojunction. The fill factor is slightly lower due to a higher series resistance in the S-TiO$_2$ case. This is consistent with less efficient charge transfer from the highly doped AZO to the S-TiO$_2$ (Appendix 5- Figure SI 15 and 16).

In the smaller-bandgap cases, a more delicate balance is found. The use of the S-TiO$_2$ electron acceptor not only reduces short circuit current, but also removes the charge transfer effect, leading to an unacceptably S-shaped J-V characteristic. Only when the optimally aligned M-TiO$_2$ is employed do the 1.0 eV bandgap devices achieve their best >4% AM1.5 efficiency performance.

![Figure 33 J-V characteristics under AM1.5 illumination of PbS CQD devices made on M-AZO followed by both S-TiO$_2$ and M-TiO$_2$; we show that M-TiO$_2$ is optimal for 1.1 and 1.3 eV CQD having a deeper LUMO and thus a lower barrier height than 1.3 eV CQD.](image)

Figure 33 J-V characteristics under AM1.5 illumination of 1 (red), 1.1 (green) and 1.3 eV (blue) PbS CQD devices made on M-AZO followed by both S-TiO$_2$ and M-TiO$_2$; we show that M-TiO$_2$ is optimal for 1.1 and 1.3 eV CQD having a deeper LUMO and thus a lower barrier height than 1.3 eV CQD. Reprinted with permission from Nano Letters$^{66}$ Copyright 2011 American Chemical Society.

Figure 34 illustrates the optimal prescription for a DSE-based contact to a p-type CQD PV device. The use of a mild but still favorable band offset from the CQD layer to the TiO$_2$, such as
0.1 eV, aids injection of photoelectrons and minimizes bimolecular recombination (Figure 34c). The use of a conductive AZO layer whose work function matches that of this TiO₂ leads to charge-transfer doping and favorable band bending including at $V_{oc}$.

![Figure 34](a) Band diagram and (b) J-V characteristics of 1 eV CQD device made on S-AZO followed by S-TiO₂ next to one made on M-AZO followed by M-TiO₂; the latter has a favorable band offset that increases carrier injection and reduces back-surface recombination depicted by intensity dependent $J_{sc}$ measurement in (c). Reprinted with permission from Nano LettersCopyright 2011 American Chemical Society.

The prescription is thus:

a. $\varphi$ (TiO₂) slightly deeper than the conduction band-edge of the CQD layer to favor injection

b. $\varphi$ (AZO) slightly shallower than $\varphi$ (TiO₂) to favor charge transfer doping
In summary, we showed the successful utilization of the donor-supply electrode in colloidal quantum dot photovoltaics. With the insertion of a highly doped well-aligned layer beneath the resistive sputtered TiO₂, electrons from the AZO help to overcome the low doping, depletion, and low mobility seen in the thin sputtered TiO₂. The resultant electrodes are compatible with room-temperature processing, advantageous in integration with transparent flexible substrates, and with temperature-sensitive prior layers such as those employed in a tandem colloidal quantum dot solar cell. Colloidal quantum dot devices having a bandgap of 1.0 eV, suitable as the back cell in tandem photovoltaics, achieve 4% solar power conversion efficiencies and fill factor exceeding 55% when coupled to a suitably chosen DSE.

5.3. Conclusions

In chapter 5, the development of the constituent single junctions of a CQD tandem solar cell, the visible and the infrared cell, was discussed.

With a properly selected band offset between the electron accepting electrode and the 1.6 eV PbS CQD, favorable injection of electrons into the TiO₂ occurs. Employing a deeper work function ohmic contact, MoO₃, provides improved performance.

We also established that the back cell of a CQD tandem cell needs to be processed at low-temperature for thermal compatibility with prior deposited layers in the tandem structure. Simply replacing the high-temperature-processed TiO₂ employed in previously reported high efficient PbS CQD solar cells with a sputtered version of the same material leads to poor performance due to the extremely low mobility in conjunction with the low doping of the sputtered oxide. We developed an electrode strategy where we employed a two-layer donor-supply electrode in which a highly doped, shallow work function layer supplies a high density of free electrons to an ultrathin TiO₂ layer via charge-transfer doping. For optimal performance, the work function of the TiO₂ needs to be slightly deeper than the conduction band-edge of the CQD layer to favor injection without compromising the $V_{oc}$, and the work function of the highly doped AZO needs to be slightly shallower than that of the TiO₂ to favor charge transfer doping.

We describe in chapter 6 the integration of the above developed single junctions into a tandem solar cell connected through a graded recombination layer.
Chapter 6 CQD Tandem Solar Cell

We established in chapter 3 that tuning of the electronic bandgap in CQDs by changing their size enables the spectral response of CQD-based photodetectors\textsuperscript{80–84} and photovoltaic\textsuperscript{11,18,23,37,38,48,85,86} devices to be tailored. Multijunction solar cells made from a combination of CQDs of differing sizes and thus bandgaps are a promising means by which to increase the energy harvested from the sun’s broad spectrum. We described in chapter 5 the development of efficient visible and infrared PbS CQD solar cells that can be directly integrated into a tandem structure. In the following chapter, we present the first CQD tandem solar cells using the size-effect tuning of a single CQD material, PbS. We describe our recombination layer strategy that employed a progression of work functions from the hole-accepting electrode in the bottom cell to the electron-accepting electrode in the top cell, allowing matched electron and hole currents to meet and recombine.\textsuperscript{21,87}

6.1. Introduction

The capacity to tune the bandgap of CQDs allows tandem and multijunction cells to be realized, devices that raise the ultimate limit on solar cell performance. Herein, we report the construction of an efficient recombination layer that is tailored to the requirements of CQD photovoltaics, and we deploy this new technology to demonstrate the first tandem CQD photovoltaic devices. We current-match and stack two depleted heterojunction CQD solar cells (Figure 35). We use colloidal quantum dots having exciton peaks at 1.6 eV for the visible junction (front cell) and 1 eV for the infrared junction (back cell) (Fig. 36 a,b). These bandgaps are within 5\% of optimal for a current-matched solar cell.\textsuperscript{25,37}
In current-matched series-connected tandem solar cells, the hole current from the front cell and the electron current from the back cell must recombine with high efficiency and minimal loss of electrical potential in a suitably designed intervening layer. In epitaxial compound semiconductor devices this is achieved using tunnel junctions\textsuperscript{57,59,88,89} and in organic photovoltaics using recombination layers.\textsuperscript{14,60} CQD solids (or materials of similar bandgap and compatible with CQD processing) that achieve the sequential combination of transparent p++ followed by n++ doping are not available.
Figure 36 Colloidal quantum dot based tandem solar cells: concept and realization. Device architecture (a) and spectral utilization (b) for CQD tandem solar cells having quantum-confined bandgaps of 1.6 eV (green) and 1.0 eV (red). c–e, Spatial band diagrams for CQD tandem cells at equilibrium (c) and under short-circuit (d) and open-circuit (e) conditions, where $E_F$ is the Fermi energy (dashed-dotted line in c), $E_{F_n}$ is the electron quasi-Fermi energy (dashed line in d and e), and $E_{F_p}$ is the hole quasi-Fermi energy (dotted line in d and e).

We sought a new strategy that would be compatible with CQDs, and that would enable the realization of a highly effective tandem solar cell. We term this new concept a ‘graded recombination layer’. We present a practical GRL design using spatial band diagrams to depict a CQD tandem cell at equilibrium (Figure 36c), and under short-circuit (Figure 36d) and open-circuit conditions (Figure 36e).
6.2. The Graded Recombination Layer

Photoholes from the valence band of the front cell are required to recombine with photoelectrons from the conduction band of the back cell. They must do so without adding appreciably to the series resistance of the overall device. If the deep-work-function contact associated with the front cell were directly connected to the shallow-work-function electron-acceptor of the back cell, a large energetic barrier would impede the flow of electrons necessary for recombination with the holes from the front cell.

The GRL concept overcomes this problem by using a progression of work functions from the front to the back cell. The concept is implemented using a progression of n-type transparent oxides\(^70,90,91\) that are both readily available and CQD-compatible. We progress from deep-work-function n-type MoO\(_3\) through intermediate indium tin oxide (ITO) to shallow-work-function but still heavily doped AZO, the work function of which matches that of the lightly doped TiO\(_2\) acceptor. All these materials are deposited using room-temperature sputtering processes compatible with CQD films.

Ideally, the gradual progression of the GRL would achieve barrier-free conveyance of electrons from the back cell to recombine with the holes extracted from the front cell. In our actual devices, relatively small barriers can be seen in Figure 36c–e. From calculations (refer to chapter 7) and the experiments reported here, we find that these barriers are sufficiently readily overcome to allow the GRL to have a series resistance that is sufficiently low to enable a solar cell operating at 1 sun.

6.3. Current Matching

Current matching is also required in an optimized tandem cell; the absorbed photon spectrum should be divided equally between the two junctions to match the currents meeting up in the recombination layer. We first measured the absorbance spectrum of PbS CQD films and obtained their absorption coefficients (Figure 37a). We then determined the total current density from the 200-nm thick front cell when the internal quantum efficiency averaged 70% (Figure 37b and Appendix 6). Figure 37b plots the expected current density of the back cell as a function of its thickness when the IQE averages 35% (Appendix 6). This plot predicts that a back-cell thickness in the range 250–300 nm should achieve current matching.
Device Performance

To verify these calculations, we built a 300-nm-thick infrared wavelength cell having the usual reflective top contact, and illuminated it through a transparent-top-contact visible-wavelength cell. In this configuration we measured a $J_{sc}$ of 8.7 mA cm$^{-2}$ and 8.9 mA cm$^{-2}$ (Figure 38a) for the visible and infrared cells. This confirmed that our model had enabled us to achieve current matching to within a few percent.
Figure 38 Photovoltaic device performance for tandem and constituent single-junction cells. a, Current–voltage characteristics under AM1.5 1 sun simulated illumination for the large-bandgap (blue) and small-bandgap (black) cells. J–V of the small-bandgap device when the large-bandgap CQD film is used as a filter is also shown (red). The tandem cell J–V is shown in green. b, EQE spectra of the large-bandgap junction with a transparent top contact (blue), the small-bandgap junction with a reflective top contact (black), and the small-bandgap junction with the large-bandgap CQD film used as filter (red). When the large-bandgap CQD film filters the incoming light, the estimated $J_{sc}$ of the small-bandgap junction is matched to the $J_{sc}$ of the large-bandgap junction.

Figure 38a presents the measured current–voltage characteristics of the constituent junctions and the tandem cell under 100 mW cm$^{-2}$ AM1.5 illumination. Table 5 summarizes the figures of merit of our devices. The single-junction visible device (with transparent top contact) exhibits an open-circuit voltage $V_{oc1}$ of 0.7 V, $J_{sc}$ of 8.7 mA cm$^{-2}$, fill factor of 49% and AM1.5 power conversion efficiency of 2.98%. The single-junction infrared device exhibits an open-circuit
voltage $V_{oc2}$ of 0.39 V, $J_{sc}$ of 18.6 mA cm$^{-2}$, FF of 42% and AM1.5 PCE of 3.04%. When the visible CQD film is used as a filter, the IR cell $J_{sc}$ drops to 8.9 mA cm$^{-2}$. The ideal tandem cell should exhibit a $V_{oc}$ equal to the sum of the open-circuit voltages of the constituent cells. The GRL device achieves an open-circuit voltage of 1.06 V, equal, to within a few percent, to the sum of the open-circuit voltages of the individual single junctions. The tandem CQD photovoltaic device provides an AM1.5 PCE of 4.21%, compared to the ~3% values achieved by its constituents. Further J-V characteristics are included in Appendix 7.

Table 5 Figures of merit of the devices cell under 100 mWcm$^{-2}$ AM1.5 illumination.

<table>
<thead>
<tr>
<th>Junctions</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visible</td>
<td>8.7</td>
<td>0.7</td>
<td>49</td>
<td>2.98</td>
</tr>
<tr>
<td>IR</td>
<td>18.6</td>
<td>0.39</td>
<td>42</td>
<td>3.04</td>
</tr>
<tr>
<td>IR/Visible filter</td>
<td>8.9</td>
<td>0.36</td>
<td>46</td>
<td>1.47</td>
</tr>
<tr>
<td>Tandem</td>
<td>8.3</td>
<td>1.06</td>
<td>48</td>
<td>4.21</td>
</tr>
</tbody>
</table>

The external quantum efficiency spectra (Figure 38b) of the constituent single-junction solar cells further confirm current matching. The integrated current density of the visible-junction (area under blue curve) was calculated to equal, within 10%, the integrated current density of the IR junction filtered by the visible junction (area under red curve).

As a control, we constructed a tandem device that does not benefit from the GRL. This device directly connected MoO$_3$ and TiO$_2$. It exhibited a much lower open-circuit voltage of 0.76 V as well as a weakened short-circuit current compared to the GRL device. We attribute this suboptimal behaviour to the establishment of an undesired barrier to electron flow in the intended cascade from TiO$_2$ to MoO$_3$ (details in chapter 7).

6.5. Electrical Properties of the GRL Constituent Materials

We now discuss further the processing and properties of the layers that constitute the GRL. To maintain their performance (for example, low recombination rates) CQD films require a minimum of exposure to reactive oxygen. A layer (10 nm) of MoO$_3$ was first evaporated onto the CQD films, serving both as the deep-work-function n++ layer and as a buffer layer to protect against damage during ensuing layer depositions. We designed the layers constituting the GRL to be as thin as possible to minimize parasitic electrical losses while still ensuring complete
coverage of the prior layers. We selected 10 nm, 50 nm, 50 nm and 40 nm for the MoO$_3$, ITO, AZO and TiO$_2$ layers, respectively.
Figure 39 Electrical characterization of GRL materials. a, UPS data for MoO$_3$, AZO and TiO$_2$ and FET transconductance for MoO$_3$, AZO and TiO$_2$. b, Energy level diagram showing the HOMO and LUMO energies of each type of PbS quantum dot, and the Fermi levels (dashed lines) and band edges of the isolated GRL materials.

A detailed electronic materials characterization (Figure 39) of MoO$_3$, AZO and TiO$_2$ is now presented. Table 6 summarizes the measured electron affinity $E_c$, work function $E_f$, ionization energy $E_v$ and electron free-carrier density $n_0$ of the metal oxides. Ultraviolet photoelectron spectroscopy (UPS) was used to obtain work functions (Appendix 2 – Figure SI 2, 3 and 4). The work functions progress from 5.4 eV (MoO$_3$) through 4.8 eV (ITO) to 4.1 eV for both AZO and TiO$_2$. Band edges were also obtained using UPS. For AZO and TiO$_2$, electron affinities of 4.1 and 4.0 eV, respectively, were measured. We confirmed these values using cyclic voltammetry, which provided the electron affinities directly by means of an alternative measurement (Appendix 3 – Figure SI 9).

Table 6 Electrical properties of the GRL constituent materials.

<table>
<thead>
<tr>
<th></th>
<th>$E_f$ (eV)</th>
<th>$E_v$ (eV)</th>
<th>$E_c$ (eV)</th>
<th>$n_0$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$_3$</td>
<td>5.4</td>
<td>8.5</td>
<td>5.4</td>
<td>$\sim 10^{19}$</td>
</tr>
<tr>
<td>ITO</td>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZO</td>
<td>4.1</td>
<td>7.4</td>
<td>4.1</td>
<td>$\sim 5 \times 10^{19}$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>4.1</td>
<td>7.7</td>
<td>4.0</td>
<td>$\sim 5 \times 10^{16}$</td>
</tr>
</tbody>
</table>

$E_f$ work function; $E_v$ ionization energy; $E_c$ electron affinity; $n_0$ electron free-carrier density.
Field-effect transistor (FET) test structures were constructed to estimate the carrier densities. Doping values of $\sim 1 \times 10^{19}$ and $\sim 5 \times 10^{19}$ cm$^{-3}$ for MoO$_3$ and AZO, respectively, confirmed that they are heavily doped materials, and the doping value of $\sim 5 \times 10^{16}$ cm$^{-3}$ for TiO$_2$ confirms its light doping. We found that conduction band-edge values obtained from cyclic voltammetry varied by $\pm 50$ meV from run to run. Mobility and doping values were consistent run to run, within one order of magnitude.

More than 100 tandem CQD solar cells were made in developing the fabrication process, with the best device demonstrating an efficiency of 4.2%. In the course of these studies, we fabricated more than 20 devices with efficiencies greater than 3%.

### 6.6. Summary

Grading of stoichiometry, and thus band-edge position, is a concept widely used to great effect in semiconductor quantum electronics, including ultrahigh-frequency heterojunction bipolar transistors$^{92}$ and graded-index separate-confinement-heterostructure lasers with low lasing thresholds.$^{93}$ The work presented in this chapter showcases the benefit to work-function grading and the attractiveness of grading strategies in soft materials such as organic small molecules, polymers and CQDs. The GRL concept can be used to build photovoltaic devices with three or more junctions. Such many-junction devices provide a route to overcoming the charge carrier transport limitations in CQD films today, and, more broadly, they offer the potential to reach well above the Shockley–Queisser limit.

In chapter 7, we investigate the generalized conditions for the design of efficient graded recombination layers in multijunction solar devices. We determine the number of graded layers that constitute the GRL and their required work function and doping, enabling the efficient connection of a work function difference as high as 1.6 eV.$^{87}$
Chapter 7 Graded Recombination Layers for Multijunction Photovoltaics

Chapter 6 presented a tandem solar cell in which the recombination layer was implemented using a progression of n-type oxides whose doping densities and work functions serve to connect, with negligible resistive loss at solar current densities, the constituent cells. In chapter 7 we present generalized conditions for the design of efficient graded recombination layers for multijunction PV devices. We report the number of interlayers and the required work function and doping of each interlayer, to bridge a band offset difference as high as 1.6 eV. We also present alternatives that minimize the doping required of the interlayers in order to minimize infrared optical absorption due to free carriers in the GRL. We demonstrate a family of new GRL designs experimentally and highlight the benefits of the progression of dopings and work functions in the interlayers.

7.1. Introduction

Efficient transparent intermediate layers sandwiched between the junctions are essential to a current-matched multijunction solar cell. They allow the photogenerated electrons and holes from adjacent junctions to meet and recombine efficiently with minimal optical and electrical loss as described in chapter 6. In traditional epitaxial compound semiconductor multijunction solar cells,\textsuperscript{89} extremely thin (2-5 nm) tunnel junctions formed by p++ and n++ interface are employed for this purpose. Since low temperature-processed degenerately doped metal oxides represent a challenge in materials processing, solution-processed organic and inorganic cells require innovative solutions. In organic photovoltaics, multijunction solar cells employ recombination layers: electrons and holes recombine in metal nanoparticles inserted between the electron-transport and hole-transport layers.\textsuperscript{60}

We reported in chapter 6 a tandem solar cell employing a new recombination layer (GRL) design tailored to be compatible with room-temperature processing (Figure 40a).\textsuperscript{21} In the GRL, a progression of readily available n-type transparent conductive oxides connects the front cell to the back cell.
7.2. GRL Design

The concept underlying the GRL is as follows: If a deep work function ohmic electrode (OE) to the front cell were directly connected to a shallow work function electron acceptor in the back cell (Figure 40b,c), a large energetic barrier would block the flow of electrons. This would prevent efficient recombination of these electrons with the holes generated in the front cell. This large energetic barrier for electrons could be reduced by building a continuously graded recombination layer that would connect the junctions and present no barrier to the flow of charge carriers (Figure 40d). Unfortunately, such a material - one that would continuously span the entire 1 eV work function separation of interest - is not readily available.

A more realistic strategy would employ a discrete set of intervening layers (IL1, 2, ...), each having an appropriate doping level, work function, and conductivity. This would enable electrons to flow across the recombination layer with an acceptable resistance in a photovoltaic device context (Figure 40e). For ease of experimental implementation, the approach would rely on transparent conductive n-type oxides having doping levels in the range of $10^{16} - 10^{21}$ cm$^{-3}$ work functions in the range 4–5 eV, such as TiO$_2$, ZnO, AZO, ITO, SnO, ZIO, TIO, TZO, and MIO.\textsuperscript{21,66,73,91,94–96}
Figure 40 (a) Schematic of a colloidal quantum dot tandem solar cell employing a GRL. The GRL purposes to enable low-impedance connection of the deep work function ohmic electrode (OE) of the front cell with the electron acceptor of the back cell. (b) Equilibrium spatial band diagram for the case of direct contact with the low-doped shallow work function (TiO$_2$). A thick, higher barrier to electron flow is formed. (c) When a donor-supply electrode is instead employed, a high tunneling barrier prevents electron flow. (d) An ideal
continuously graded recombination layer would eliminate all barriers to electron flow. (e) More realizably, using multiple graded intervening layers of appropriate doping and work functions allows electron transport across the energetic barriers with acceptor resistance for solar applications. Reprinted with permission from Nano Letters\textsuperscript{87} Copyright 2012 American Chemical Society.

We sought to quantify the requirements for an efficient GRL that connects subcells separated by energy barriers ($\Delta \phi$) in the range of 1–1.6 eV. We assumed that the deep work function hole contact (OE) and the shallow work function electron acceptor both had free carrier densities in the $10^{19} \text{ cm}^{-3}$ range.\textsuperscript{21,66} In our modeling, we accounted for two additive contributors to current density over or through a barrier:

1. The tunneling current,\textsuperscript{97} described via the Fowler-Nordheim equation $J = \lambda a \varphi_b^{-1} F^2 \exp(-\mu b \varphi_b^{3/2}/F)$, where $a \sim 1.5 \times 10^{-6} \text{ A eV}^{-2}$ and $b \sim 6.8 \text{ eV}^{3/2} \text{ V nm}^{-1}$, $\lambda = 1$, $\mu = (m_e^*/m_e)^{3/2}$, and $eF = \varphi_b/x_d$, where $\varphi_b$ is the barrier height and $x_d$ is the barrier width. Tunneling tends to dominate in the case of narrow barriers, a condition facilitated by the use of high doping levels ($\sim 10^{18} \text{ cm}^{-3}$). Tunneling will be the dominant mode of transport in designs that employ a small number of highly doped intervening layers separated by high barriers ($\sim 0.3 \text{ eV}$).

2. The thermionic emission current density, described by equation $J = A^{**} T^2 \exp(-e \varphi_b/kT) \exp(V/nkT) - 1$, where $A^{**}$ is the Richardson constant, $\varphi_b$ is the barrier height, $n$ is the ideality factor of the diode. To pass solar current densities through the thermionic mechanism with acceptably low resistance, the barrier height $\varphi_b$ must typically be less than ~0.3 eV. Thus a thermionic approach to a graded recombination layer strategy will employ a significant number of low-doped intervening layers, where the total barrier height is divided evenly among the multiple layers.

The modeling reported in this work does not take into account the traps and the interface states that could be present and that could pin the energy levels regardless of the electrical properties of the oxides employed. However, we are assuming that the oxides will behave close to ideal conditions similar to the behavior of the DSE electrode presented in chapter 5 whereby the interfaces between ITO and TiO$_2$ and between AZO and TiO$_2$ were consistent with our modeling results.
7.2.1. GRL with a Single Intervening Layer

The details of our modeling assumptions are provided in Appendix 8. The materials and spatial band diagrams before contact and at equilibrium are shown in Figure 41a,b.

Figure 41 Energy level diagrams of a GRL designed with one intervening layer IL1: (a) before being brought into contact and (b) at equilibrium. (c) The required IL1 doping density \( N_{D1} \) for a range of work functions \( W_{F1} \) to sustain 1 sun with minimal electrical potential loss (0.01 V). The model considered the cases of total work function differences, hence total combined barrier heights \( \Delta \phi \), of 1, 1.2, and 1.4 eV. For larger energy
separation, one intervening layer is not viable. The different emission modes across \( \phi_{B1} \) are depicted in the figure and explained in the text. Reprinted with permission from Nano Letters\(^{87} \) Copyright 2012 American Chemical Society.

We sought first to determine the design, using a single intermediate work function layer, that would minimize, as much as possible, the doping density required. This would expand the range of practical n-type oxides that could usefully be employed while also minimizing free carrier absorption. Figure 41c reports the interlayer doping \( N_{D1} \) required, as a function of the work functions (\( W_{F1} \)) of the intervening layer, to allow a 1 sun (\( J \sim 25 \text{ mA/cm}^2 \)) to be conveyed with negligible resistive losses. Specifically, to lose less than 0.01 V of operating voltage under solar current densities, \( R^*A = V/J < \sim 1 \Omega \cdot \text{cm}^2 \), with \( R \) being the resistance and \( A \) the device area. We considered the cases of work function differences \( \Delta \phi \) of 1, 1.2, and 1.4 eV.

We now discuss the principles for selecting an interlayer work function that minimizes the required interlayer doping. As seen in Figure 41a, electrons flowing from the back to the front cell face two barriers in series, \( \phi_{B1} \) and \( \phi_{B2} \). Electron transport through \( \phi_{B1} \) is determined by the free carrier density and work function of the shallow work function electron acceptor. It is purely thermionic when \( \phi_{B1} \) is small (<0.25 eV). Thermionic and tunneling components become comparable to one another for 0.25 < \( \phi_{B1} \) < 0.45 eV. Tunneling dominates in the range 0.45 < \( \phi_{B1} \) < 0.75 eV. For the chosen DSE doping level, solar currents can no longer transit the first barrier when its height exceeds \( \phi_{B1} \) of 0.75 eV. The preceding limitations ensure that the second barrier \( \phi_{B2} \) will always exceed >0.25 eV. As a result of this fact, combined with the high doping required in the single interlayer case, (> \( 10^{19} \text{ cm}^{-3} \) for \( \Delta \phi \geq 1 \text{ eV} \)), transport across the second barrier is dominated by tunneling.

We built and characterized (Figure 42) photovoltaic devices employing the single intervening layer GRL design. We used a single ITO intervening layer, thereby implementing the case \( \Delta \phi \sim 1.3 \text{ eV}, \phi_{B1} \sim 0.7 \text{ eV}, \text{and} N_{D1} > 10^{19} \text{ cm}^{-3} \) (Figure 41a band diagram, Appendix 8). When we replaced the ITO layer with 1 nm metallic Ag nanoclusters, we achieved a slightly higher performance with lower series resistance, consistent with the \( W_{F1} = 4.5 \text{ eV} \) case of Figure 41a and the extremely high carrier free carrier density in metallic Ag. Much lower performance results when we employ Au nanoclusters, a fact we attribute to its deeper work function that causes the first barrier to exceed the 0.75 eV threshold for efficient solar operation. We included
a control in which we connect the front and back cells directly. A catastrophic loss in performance results: An S-shape curvature is obtained, lowering the open circuit voltage to less than 1 V and the fill factor to less than 30%.

![Energy levels of different intervening layers](image1)

![J-V characteristics](image2)

**Figure 42** Experimental results. (a) Energy levels of different intervening layers employed in CQD tandem solar cells, and (b) J– V characteristics of the CQD tandem solar cells without any intervening layers and with ITO, thin Au, and thin Ag as the intervening layer connecting the DSE to MoO$_3$. Reprinted with permission from Nano Letters$^{87}$ Copyright 2012 American Chemical Society.

The thin metallic and the ITO interlayers achieve similar performance and are both options of interest. While it achieved the highest performance, the sub-nanometer thick silver layer has a narrow process window to achieve nanoscale islands. This can result in run-to-run variation, and increasing its thickness to widen this window leads to a failure to fulfill the transparency requirement.$^{98}$ Furthermore, metallic layers employed in intermediate layers have been reported to diffuse into the active material of the subcells, leading to loss of high shunt resistance.$^{99}$ For these reasons, optimized transparent conductive oxide based interlayer strategies merit further consideration.

In addition, in the modeling in Figure 41, we found that work function differences greater than 1.4 eV cannot successfully be spanned using a single intervening layer.
7.2.2. GRL with Multiple Intervening Layers

We therefore explored multiple interlayer strategies that would reduce significantly the doping requirement on the intervening layers and expand the range of work function differences that can be connected. We were particularly interested in lowering the required doping down to the \( \sim 10^{16} \) cm\(^{-3}\), that is easily attained using available low-temperature deposited n-type oxides.\(^{21,66,73,91,94–96}\)

When a pair of interlayers is employed (Figure 43) and when the second interlayer uses a modest doping of \( \sim 10^{16} \) cm\(^{-3}\) and a low barrier height \( \phi_{B3} \) of 0.2 eV, efficient and purely thermionic emission is achieved across \( \phi_{B3} \). Now, for a work function difference \( \Delta \phi \) of 1 eV between the cells, two intervening layers of doping density \( \sim 10^{16} \) cm\(^{-3}\) are sufficient to sustain solar current densities.
Figure 43 GRL with two intervening layers. Energy level diagrams of a GRL designed with two intervening layers IL1 and IL2 (a) before contact and (b) at equilibrium. With IL2 work function and doping density (~10^{16} \text{ cm}^{-3}) fixed to ensure thermionic emission across $\phi_{B3}$, we plot (c) the required IL1 doping density ($N_{D1}$) for a range of work functions $W_{F1}$ to sustain 1 sun with minimal electrical potential loss (0.01 V). Modeling was done for a total energy barrier separation $\Delta \phi$ of 1, 1.2, 1.4, and 1.6 eV. For 1 eV $\Delta \phi$, thermionic emission across $\phi_{B2}$ with minimal $N_{D1}$ required of 10^{16} \text{ cm}^{-3} occurs for limited values of $W_{F1}$. Thus, two intervening layers are the maximum number of ILs needed for a 1 eV $\Delta \phi$. Reprinted with permission from Nano Letters \textsuperscript{87} Copyright 2012 American Chemical Society.

We proceeded to ascertain the number of interlayers required to enable solar currents to transit larger 1.2, 1.4, and 1.6 eV interjunction barriers using modestly doped interlayers. For $\Delta \phi$ of 1.2 and 1.4 eV, four intervening layers are sufficient, while five are necessary for a 1.6 eV energy separation (Figure 44c–f). For the 1.2 eV $\Delta \phi$ case, four intervening layers (Figure 44d) allow for purely thermionic emission across the entire GRL including $\phi_{B1}$, which for smaller numbers of interlayers is tunneling dominated.

It was assumed until this point that the back cell is contacted using a highly doped shallow work function contact. The use of multiple interlayers can also relax this requirement. Adding one extra interlayer can ensure that thermionic emission occurs across all barriers including $\phi_{B1}$ and obviate the need for the heavily doped donor-supply electrode.\textsuperscript{66}
7.2.3. Optical Transmission Considerations

We now evaluate the benefits, in terms of optical transmission in the infrared spectral region, that are accrued when low-doped intervening layers (with reduced free carrier absorption) are employed (Appendix 8). As seen in Table 7, considering the case of $\Delta \phi$ larger than 1.2 eV, the use of 1 or 2 intervening layers demands a high doping ($>10^{19}$ cm$^{-3}$), which leads to high optical loss. Replacing the highly doped layers with multiple low-doped layers (Figure 45) reduces optical loss appreciably. Only by using a GRL consisting of at least 3 intervening layers can optical loss through the GRL be kept below 5% for large work function differences $\Delta \phi$ of 1.6 eV or greater.
Figure 45: Optical transmission, parameterized as a function of the number of intervening layers employed, for the different GRL designs summarized in Table 7. Reprinted with permission from Nano Letters. Copyright 2012 American Chemical Society.
Table 7 Summary of the design rules of GRLs sustaining solar intensities at minimal photovoltage loss. Reprinted with permission from Nano Letters\textsuperscript{87} Copyright 2012 American Chemical Society.

<table>
<thead>
<tr>
<th>$\Delta \phi$ (eV)</th>
<th>$N_D$ required (cm$^{-2}$) of</th>
<th>$t_{\text{per layer}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IL.1</td>
<td>IL.2</td>
</tr>
<tr>
<td>1</td>
<td>$6.3 \times 10^{17}$</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>$10^{16}$</td>
<td>$10^{16}$</td>
</tr>
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<td>1.2</td>
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<td>...</td>
</tr>
<tr>
<td></td>
<td>$1.2 \times 10^{18}$</td>
<td>$10^{16}$</td>
</tr>
<tr>
<td></td>
<td>$2.4 \times 10^{18}$</td>
<td>$10^{16}$</td>
</tr>
<tr>
<td></td>
<td>$10^{16}$</td>
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<td>$4 \times 10^{17}$</td>
<td>...</td>
</tr>
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<td>$10^{16}$</td>
</tr>
<tr>
<td></td>
<td>$10^{16}$</td>
<td>$10^{16}$</td>
</tr>
</tbody>
</table>

$^5$Thickness per layer. $^6$Tunneling mode through $\phi_{B_2}$

7.3. Summary

In chapter 7, we summarized the design of an efficient GRL of interest in a variety of solution-processed solar cells, including colloidal quantum dot and organic photovoltaics. To achieve high transmittance and a wide process window, intervening layers based on low-doped oxides, with their low free carrier absorption, are desired. A work function difference of 1 eV can be spanned in a number of ways. A single optimal work function interlayer is sufficient but relies on a relatively high doping of $1 \times 10^{19}$ cm$^{-3}$. A pair of interlayers having a much lower $1 \times 10^{16}$ cm$^{-3}$ can efficiently span this work function difference. Adding a further interlayer can obviate the need for the highly doped donor-supply electrode. Higher numbers of interlayers allow successful spanning of larger work function differences using the same principles. Selection of work functions of these interlayers according to the prescriptions of this work is readily implemented using the wide range of room-temperature deposited conductive oxides in the literature.
Chapter 8 Summary and Conclusions

This chapter summarizes the major research findings of this dissertation and discusses this work’s contributions to the field and future research directions.

8.1. Thesis Objectives

We answered the research questions posed in chapter 1 throughout the thesis. We will revisit each question and answer it in the context of our research findings.

8.1.1. CQD Spectral Tunability

- *Is it possible to fabricate efficient photovoltaic devices of varying size to achieve selective spectral tunability?*

We employed 1.6 eV and 1 eV PbS CQD dots to fabricate the front and back cell of a tandem solar cell. In chapter 4, we described the processing of both quantum dot sizes; through simple modifications of the synthesis process, different sizes are obtained. In chapter 5, we demonstrated 1.6 eV and 1 eV PbS CQD single junction solar cells with efficiencies of 3.5 and 4% respectively.

- *Will we need to conduct material processing modifications for the different sizes? Will those modifications render them incompatible for monolithic integration?*

We successfully modified our layer-by-layer deposition technique for each size of quantum dot which led to record single-junction performances. In particular, the crosslinking treatment concentration was optimized for each CQD size. In chapter 4, we described the details of the deposition techniques that lead to enhanced morphology necessary for higher performance in tandem structures. We were able to successfully employ our modified recipes for monolithic integration; current matching conditions dictated that 200 nm of the visible 1.6 eV PbS CQD and 300 nm of the infrared 1 eV PbD CQD were necessary in the tandem structure.
8.1.2. Design of 1.6 and 1 eV Single Junctions CQD Solar Cells

- What are the design specifications we need to consider to maximize electron injection from the 1.6 eV PbS CQD without compromising the open circuit voltage of the solar cell?

In chapter 5, we presented the methodology we adopted to optimize the performance of the visible junction. Employing a ~3.8 eV work function electron accepting electrode we enhanced the electron injection from the 1.6 eV PbS CQD with optimal open circuit voltage of 0.7 V. We also replaced Au as an ohmic contact with a deep work function oxide MoO$_3$; the better alignment with the HOMO level of the PbS CQD led to higher performance.

- How would the inclusion of an infrared 1 eV layer be possible atop the front cell of a tandem structure? Would a simple replacement of the electron accepting electrode with its room-temperature processed counterpart lead to efficient devices?

We also reported in chapter 5 the DSE strategy we adopted to fabricate efficient infrared room-temperature processed PbS CQD single junctions. Prior to this work, all the single junctions reported in literature utilized high-temperature-processed electrodes rendering them incompatible to be employed in a tandem structure. We found that replacing the high temperature processed TiO$_2$ with its sputtered counterpart led to highly resistive devices. Employing the highly doped and conductive shallow work function electrode AZO did not solve the problem either; we attributed this issue to incompatibility of AZO with the PbS CQD surface. We sought to combine the TiO$_2$ with the AZO in such a way that the highly doped electrode serves as an underlayer and thus enables charge transfer to the lower doped TiO$_2$. We found that the conditions for successful charge transfer, and thus efficient room-temperature processed PbS CQD devices depend on the positions of the conduction band edge of the PbS CQD, and the work functions of both the TiO$_2$ and AZO layers.

8.1.3. The First CQD Tandem Solar Cell

- How can we build a recombination layer that efficiently brings the electrons from the back cell to the holes from the front cells without loss and that is at the same time room-temperature CQD processing compatible?
We describe the fabrication of a CQD tandem solar cell in chapter 6. We employed a graded recombination layer to efficiently connect the front cell and the back cell of the tandem junction. With a progression of work function of the n-type oxides connecting the LUMO level of the infrared PbS CQD solar cell to the HOMO level of the visible CQD junction, we were able to provide a barrier-free pathway for electrons of the back cell to recombine with the holes of the front cell. We show evidence of current matching via modeling supported by the currents recorded. In addition, integrating the EQE spectra of both single junctions led to similar expected $J_{sc}$. The tandem solar cell had a power conversion efficiency of 4.2%, higher than both single junction’s respective performances and an open circuit voltage equivalent to the sum of that of the single junctions. We also presented the different optical and electrical properties of the n-type oxides employed within the GRL in chapter 6. Employing readily available n-type oxides with graded work functions proved to be an effective and original strategy to fabricate an efficient CQD tandem solar cell.

8.1.4. Design of GRL for Multijunction Photovoltaics.

- What are the electrical properties, i.e. work functions and doping densities, of the interlayers included in the GRL that would enable us to achieve low absorbance and photovoltage loss while still sustaining solar intensities?

We provided a detailed study in designing GRLs suitable for various multijunction applications in chapter 7. We determined how many interlayers in the GRL are necessary to sustain solar intensities and we determined the doping density and the work function of each interlayer for various work function offsets. Intervening layers based on low-doped oxides, with their low free carrier absorption, were found to be desirable. A work function difference of 1 eV can be bridged in a number of ways. A single optimal work function interlayer would in principle work but would rely on a relatively high doping density while a pair of interlayers having a much lower doping density can span this work function difference just as efficiently. Higher numbers of lower doped interlayers allow successful bridging of larger work function differences. All the interlayers within the context of our study can be implemented using readily available n-type oxides reported in literature.
8.2. Main Research Contributions

In this section, we will briefly list the main research contribution of this work.

1) In chapter 5, we reported the best performing visible PbS CQD junction engineered via careful selection of the electron accepting electrode and its ohmic contact. This accomplishment allows the possibility of triple- and multi-junction PV with maximum theoretical efficiency far exceeding that of single junctions.

2) A completely new electrode strategy employing a two-layer donor-supply electrode in which a highly doped, shallow work function layer supplies a high density of free electrons to an ultrathin TiO₂ layer via charge-transfer doping was reported in chapter 5. All previous depleted heterojunction CQD cells relied on electrodes incompatible with CQD processing. With manipulation of the sputtering environment, and modeling, we were able to optimize the charge transfer from AZO to TiO₂ leading to the best ever reported 1 eV PbS CQD solar cell performance.

3) Prior to this work, a CQD tandem solar cell was never fabricated; part of the reason was because of the unavailability of materials that could efficiently form a recombination layer connecting the front and back cell. We conceived the graded recombination layer whereby a graded series of n-type oxides connect the junctions of the tandem and allows electron injection with minimal photovoltage loss.

4) We wanted to dive deeper into the general design requirements of an ideal graded recombination layer which can sustain solar intensities with minimal photovoltage loss. Our work will benefit the growing research directed into solution-processed multijunction structures: to achieve low absorbance loss inside the recombination layer, we found that multiple graded intervening layers based on low-doped graded oxides, with their low free carrier absorption, are best suited for tandem solar cells.

8.3. Future Directions

This work represents a substantial leap forward in the design of complex CQD architectures. Before this work, only single bandgap junctions were reported in literature. The following are potential directions stemming from our work:
1) The use of multiple bandgap CQD in a single junction has various applications, not limited to photovoltaics. Multijunction light emitting devices employing organic polymers have already been reported\textsuperscript{100,101} and now multijunction CQD light emitting devices are possible. Spectral selection is one of the attractive properties of CQD and we have employed it to its full capacity paving the way for further applications in triple junction photovoltaics and thus increasing the theoretical efficiency limit up to 49\%.\textsuperscript{37}

2) We now know via our detailed study of GRL designs that multiple layers of low doping with graded work functions can serve as an efficient recombination layer. A possible future direction would be to employ solution processed material with graded work functions (such as carefully selected CQD material) either p-type or n-type and employ it as a recombination layer. A solution processed approach would circumvent costly high vacuum procedures, enable large scale roll-to-roll fabrication, and significantly improve the economic feasibility of multi-junction PV.

3) The work in this thesis aimed to raise the efficiency limit on single junction device by harnessing more of the sun’s spectrum. However, we could also increase the efficiency with light management oriented architectures such as employing nanowires as electron accepting electrodes to enhance light absorption,\textsuperscript{102} nanostructuring and plasmonics\textsuperscript{103} to enhance light trapping.

4) Another approach to raise the efficiency is to adopt a p-n heterojunction (same material system, different bandgaps) or homojunction (same material system with similar bandgaps) architecture where both the p and n regions are active regions contributing to the current. This method would allow thicker active regions, and thus higher absorption; the possibility of harnessing more of the sun’s spectrum by employing different quantum dot bandgaps in the p and n regions; and it would offer a better interface compatibility since we are employing similar material forming the p and n regions.

Major discoveries have already been made in CQD photovoltaics and all current efforts are focused on pushing the efficiency barrier further. Even though high PCEs (7\%)\textsuperscript{19,20} have been reported in single junctions, the architectures remain simple. The work reported in this dissertation describes for the first time the fabrication of a tandem CQD solar cell paving the way for further third generation CQD solar architectures. In the future we envision an optimized
multijunction CQD solar cell which employs the GRL at each junction to maximize the photovoltage and reach efficiencies that far surpass the single junction limit. With the above mentioned possible designs, major efficiency enhancements are possible in the next couple of years, bringing the field of CQD photovoltaics closer to being a commercially viable technology.
References


92. Kurishima, K., Nakajima, H., Yamahata, S., Kobayashi, T. & Matsuoka, Y. Effects of a Compositionally-Graded In_{x}Ga_{1-x}As


Appendix 1 Absorption Spectra

The results of the n-type oxides absorption measurements are shown in the graphs below. The spectra show that each material is highly transparent. We determined the optical bandgap of these materials to be 3.1 eV, 3.3 eV, and 3.4 eV for MoO$_3$, AZO and TiO$_2$, respectively. We observed a 0.3 eV discrepancy in the bandgap of TiO$_2$ obtained using UPS and cyclic voltammetry.

Figure SI 1 Optical absorption measurements of MoO$_3$, AZO and TiO$_2$.\textsuperscript{21}
Appendix 2 UPS and XPS Measurements

The full UPS spectra for MoO$_3$, AZO and TiO$_2$ are shown in chapter 6. The following plots show the regions of interest. The $E_f$ is extracted by subtracting the cut-off value of the curve from the kinetic energy of He I (21.22 eV) photon. The $E_v$ is extracted from the cut-off value of the curve, and it represents the energy below Fermi level of the material.

![Figure SI 2 Region of interest for UPS measurement of MoO$_3$.](image)

The red lines in the above two plots show the cut-off position, and UPS analysis gives values of 15.84 eV and 3.13 eV. We conclude that MoO$_3$ has $E_f$ of ~5.4 eV and $E_v$ of ~8.5 eV.

![Figure SI 3 Region of interest for UPS measurement of AZO sputtered in 1% O$_2$/Ar.](image)
The red lines in the above two plots show the cut-off position, and UPS analysis gives the value of 17.16 eV and 3.34 eV. We conclude that AZO has $E_f \sim 4.1$ eV and $E_v \sim 7.4$ eV.

Figure SI 4 Region of interest for UPS measurement of TiO$_2$ sputtered in pure Ar.

The red lines in the above two plots show the cut-off position, and UPS analysis gives the value of 17.10 eV and 3.55 eV. We conclude that TiO$_2$ has $E_f \sim 4.1$ eV and $E_v$ of $\sim 7.7$ eV.

Figure SI 5 shows the secondary electron cut-off spectra used to determine work functions as described by Helander et al. $^{104}$ of freshly prepared TiO$_2$ (1% O$_2$/Ar – red solid), TiO$_2$ (3% O$_2$/Ar – green solid) and AZO (in pure Argon – dashed blue) samples. The work functions are calculated by subtracting the cut-off binding energy of each sample (1482.48 eV for TiO$_2$-1% O$_2$/Ar, 1482.25 eV for TiO$_2$-3% O$_2$/Ar and 1482.68 eV for AZO) from the photon energy (1486.7 eV). Using this method the work functions were found to be - 4.2 eV for M-TiO$_2$, -4.45 eV for D-TiO$_2$ and -4.0 eV for S-AZO.
Figure SI 5 determining the work functions of M-TiO$_2$, D-TiO$_2$ and S-AZO.\textsuperscript{66}
The above XPS survey of MoO$_3$ shows the existence of Mo and O. Further quantitative analysis gives the atomic concentration of Mo/O=28%/72%.
The above XPS survey of AZO shows the existence of Zn, O, and Al. Further quantitative analysis gives the atomic concentration of Zn/Al=98%/2%.
The above XPS survey of AZO shows the existence of Ti and O. Further quantitative analysis gives the atomic concentration of Ti/O=31%/69%.
Appendix 3 CV Measurements

The results of the CV measurements are shown in the following figures.

![Figure SI 9 CV measurements of TiO$_2$ (in pure Ar) and AZO (1% O$_2$/Ar).]

We use the Ag/AgNO$_3$ (0.01M acetonitrile) reference electrode in the measurement, which has the absolute value of -4.7 eV. The position of the reduction peak reflects the $E_c$ of the materials. For AZO sputtered in 1% O$_2$/Ar and TiO$_2$ sputtered in pure Ar, we obtained electron affinities of 4.1 eV and 4.0 eV respectively.

The left graph in below shows the same sample went through multiple scans in CV measurement. In order to test the TiO$_2$ surface response to chemical treatment, we broke a sample into two pieces and applied chemical (MPA/methanol) treatment only on one of them. In the right graph in below, we indicated the two pieces from the same sample as ‘before chemical treatment’ and ‘after chemical treatment’. Since the sample was contaminated after CV measurement, there is a limit to test exactly the same sample before and after chemical treatment. The graph shows the electron affinity of the surface of the TiO$_2$ is not significantly affected by the MPA/methanol treatments which we use to fabricate our devices.
We further used CV to measure the electron affinity (Ec) of 2 types of TiO$_2$: in 1% O$_2$/Ar content and in 3% O$_2$/Ar.\textsuperscript{66}
Appendix 4 FET Measurements

In the following figures, our FET devices show good modulation along with applied gate bias.
The majority carrier mobility in the above mentioned oxides can be calculated using Equation 15 in 4.3.1.5; the transconductance is extracted from the slope of $I_d$-$V_g$ in the linear regime depicted in Figure 39a.

From the measured 0.2 S/cm conductivity of AZO and the extracted mobility, we estimated AZO to have a free carrier density in the mid-$10^{19}$ cm$^{-3}$ range.

From the measured $6 \times 10^{-5}$ S/cm conductivity obtained for MoO$_3$ and the extracted mobility, we estimated MoO$_3$ to have free carrier density in the low $10^{19}$ cm$^{-3}$ range.

From the measured $1.4 \times 10^{-7}$ S/cm obtained for TiO$_2$ and the estimated mobility, we estimated a doping in the mid-$10^{16}$ cm$^{-3}$ range.

In semiconductor physics, $E_f=E_c+kT\ln(N_d/N_c)$, where $N_d$ is close to the doping density $n_0$, $N_c$ is the density of states at conduction band and has the typical value of $\sim 10^{19}$ cm$^{-3}$ for wide-band gap metal-oxides. Considering the doping of our TiO$_2$ in the mid-$10^{16}$ cm$^{-3}$ range, the Fermi-level is $\sim 0.15$ eV below the conduction band edge.

We further fabricated FET devices for the three different types of TiO$_2$ mentioned in chapter 5. We show the various $I_d$-$V_g$ curves from which the mobility and doping density were determined in Figure SI 13. 

Figure SI 12 $I_d$-$V_g$ curves of MoO$_3$, AZO (sputtered in 1% O$_2$/Ar) and TiO$_2$ (sputtered in pure Ar).$^{21}$
From the measured $3.4 \times 10^{-7}$ S/cm conductivity of TiO$_2$ sputtered in pure argon and the extracted linear mobility of $3 \times 10^{-5}$ cm$^2$/V.s, we estimated this material to have a free carrier density of $7 \times 10^{15}$ cm$^{-3}$. This is well in agreement with the previous measurement.

From the measured $7.8 \times 10^{-8}$ S/cm conductivity of TiO$_2$ sputtered in 1% O$_2$ in argon and the extracted linear mobility of $1.77 \times 10^{-5}$ cm$^2$/V.s, we estimated this material to have a free carrier density of $3 \times 10^{15}$ cm$^{-3}$.

From the measured $4.2 \times 10^{-8}$ S/cm conductivity of TiO$_2$ sputtered in 3% O$_2$ in argon and the extracted linear mobility of $1.6 \times 10^{-5}$ cm$^2$/V.s, we estimated this material to have a free carrier density of $1.5 \times 10^{15}$ cm$^{-3}$. 

**Figure SI 13** $I_d$-$V_g$ curves for various TiO$_2$ types.\textsuperscript{66}
Appendix 5 SCAPS Modeling for DSE Photovoltaics

SCAPS, short for a Solar Cell Capacitance Simulator, is a 1D solar cell simulation tool developed at the University of Gent, Belgium. It was originally developed specifically for CuInSe$_2$ and the CdTe solar cell simulations. The following simulations were done using the properties reported in ref 12 concerning our TiO$_2$ and PbS dots.

Figure SI 14 Influence of ITO on thin and thick TiO$_2$
Figure SI 14 above shows the influence of the inclusion of ITO in the simulation. For thick TiO₂ ITO influence is not seen whereas when going to thin TiO₂ the influence of ITO is significant.

Figure SI 15 illustrates the charge transfer effect in a good DSE (aligned M-AZO/M-TiO₂) stand-alone structure (black) compared to the non-aligned DSE M-AZO/S-TiO₂ (red) where the charge transfer is clearly not as efficient. The total electron carrier density increases almost 2 orders of magnitude in the TiO₂ i.e. electrons are being dumped into the TiO₂.
Figure SI 16 The case of M-AZO/S-TiO₂ (red) vs. M-AZO/M-TiO₂ (blue), employing in each case 1.3 eV bandgap dots. The series resistance (R2) is lower when charge transfer occurs from the underlying AZO to the TiO₂.

Figure SI 16 depicts the modeling done for 1.3 eV dots for an electrode where DSE is in effect (blue) vs one where no charge carrier transfer occurs (red). In forward bias, the lack of charge transfer is apparent with the much lower injection.
Appendix 6 Current Matching

In order to determine the proper film thickness to achieve current matching in our structure, we considered the following in our evaluation:

- We began by fixing the thickness of the front cell at 200 nm. We had found this thickness to provide the best single-junction visible-cell performance experimentally. The average internal quantum efficiency was up to \( \sim 70\% \) in the visible region. We determined the total expected current density available from the single-junction visible-cell (with transparent top contact) to be \( \sim 9.2 \) mA/cm\(^2\).

- From the absorption coefficient of the large bandgap CQDs (figure 36a), we determined the remaining AM1.5 flux illuminating the back cell by employing the single-junction visible-cell (with transparent top contact) as the visible light filter. We found the average internal quantum efficiency of \( \sim 35\% \) for the 1.0 eV cell under the remaining AM1.5 flux. Thus we estimated the expected current density for a double-pass for various thicknesses of the small-bandgap CQD film and plotted the calculated values in figure 36b. Current matching occurs for 250-300 nm thick films.

Here, we determined the current matching conditions at \( J_{sc} \) rather than at maximum power point \( J_m \) because the fill factors of the single-junction constituents were similar in our studies as well as the degradation of the open circuit voltage to the maximum operating voltage \( (V_m/V_{oc}) \) in both single junctions. Considering the FF expression as described in equation 7

\[
FF = \frac{J_m V_m}{J_{sc} V_{oc}}
\]

the \( J_{sc} \) and \( J_m \) of both junctions are equal simultaneously if and only if the product of the FF and \( V_{oc}/V_m \) of both single junctions is equivalent. Considering our single junction performances summarized in figure 38a and table 5, the latter values are equivalent to about 5\% relative error.
Appendix 7 I-V Characteristics of Tandem CQD Solar Cells

Our tandem devices as well as single-junction solar cells need 5-10 minutes of light soaking to achieve their maximum efficiency. Similar phenomena were observed by Grätzel et al. in dye-sensitized solar cells.\textsuperscript{105} We provide in the figure below the forward and reverse scan of a typical device. The curves overlap closely, evidencing minimal hysteresis.

![Figure SI 17 Forward and reverse I-V scan of a CQD tandem solar cell; it is evident that the device shows minimal hysteresis.](image)

Below we plot the I-V characteristics of a typical device on a log-linear scale (left panel) and show the full I-V scan beyond open-circuit voltage (right panel).

![Figure SI 18 I-V curves of a tandem solar cell showing the dark characteristics and an ideality factor of 3.6 and the shape of the curve beyond open circuit voltage.](image)
Appendix 8 GRL Modeling Considerations

SCAPS Modelling

SCAPS, Solar Cell Capacitance Simulator, is a 1D self-consistent solar cell simulation tool developed at the University of Gent, Belgium. Current across a barrier has a tunnelling and thermionic component; the WKB approximation is used for the computation of the tunneling probability. Details are reported in ref 97. We constructed the entire layers constituting the GRL (DSE, intervening layers – IL1,2…, and the OE) in the model. The J-V characteristics were obtained for the various conditions. The modelling simulations were done using the properties reported in ref 17 and 23 concerning the OE and the DSE. In summary:

- DSE properties:
  1. Electron mobility = \(10^{-2}\) cm\(^2\)/V.s
  2. Electron affinity at 4.0 eV
  3. Doping density of \(5 \times 10^{-19}\) cm\(^{-3}\)
  4. Thickness of 50 nm

- OE properties:
  1. Electron mobility = \(10^{-2}\) cm\(^2\)/V.s
  2. Electron affinity at 5, 5.2, 5.4 and 5.6 eV
  3. Doping density of \(10^{-19}\) cm\(^{-3}\)
  4. Thickness of 50 nm

- Intervening Layers (ILs):
  1. Total thickness of all the ILs in each case is equal to 100 nm
2. Electron mobility = $10^{-2}$ cm$^2$/V.s

We are assuming in our modeling that a tandem junction with optimal bandgaps at 1.6 and 1 eV respectively will have to sustain approximately 25 mA/cm$^2$ current (100% EQE) in ideal 1 sun illumination conditions. In figure 40, 42 and 43, the curves indicate the minimal doping $N_{D1}$ necessary to sustain 25 mA/cm$^2$ across the GRL.

When proceeding to additional intervening layers, we optimally chose the deep work function interlayers to be 0.2 eV from each other and from the OE as indicated in figures 42 and 43, to (1) simplify the model and to (2) enable thermionic emission across all those barriers and minimizing the doping density requirement for those layers.

**Experimental Details**

We employed materials we used in chapter 6. The work functions are accurate within 0.1 eV while the doping densities are accurate to an order of magnitude.$^{21,66}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Work function (eV)</th>
<th>$N_D$ (cm$^{-3}$)</th>
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<tbody>
<tr>
<td>MoO$_3$</td>
<td>5.4</td>
<td>$10^{19}$</td>
</tr>
<tr>
<td>ITO</td>
<td>4.8</td>
<td>&gt; $10^{20}$ *</td>
</tr>
<tr>
<td>AZO</td>
<td>4.1</td>
<td>$5 \times 10^{19}$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>4.1</td>
<td>$10^{16}$</td>
</tr>
</tbody>
</table>

* widely reported to be highly doped.

**Optical loss – free carrier absorption calculations**

For near IR wavelengths ranging from 1 μm to 2 μm) the Drude–Zener theory breaks down leading to inaccurate calculations of the absorption coefficient.$^{107}$ However, the linear dependence of the free-carrier absorption $\alpha$ on the doping $N$ remains intact.$^{107}$
We assume that an oxide with a doping of $5 \times 10^{19}$ cm$^{-3}$ is estimated to have a transmission of 80% for a 100 nm thickness. From the linear dependence of $\alpha$ on $N$, we compute the optical transmission in the modeled GRL using the following equation:

$$% T = e^{-\alpha N t},$$

where $t$ is the thickness of the layer.