Gradient-Doped Thermophotovoltaic Devices based on Colloidal Quantum Dots

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Graduate Department of Electrical and Computer Engineering
University of Toronto

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Abstract

Electromagnetic radiation emitted from hot objects represents a sizeable supply of energy; however, even for relatively hot bodies, its flux peaks in the short-wavelength infrared between 1 and 3 µm, standing in the way of its photovoltaic harvest using the most widely-available optoelectronic materials such as Si and CdTe. Colloidal quantum dots combine low-cost solution-processing with bandgap tunability in this spectral region, thereby offering a route to harnessing thermal power photovoltaically. Here we report thermophotovoltaic devices constructed using colloidal quantum dots that harvest infrared radiation from an 800°C blackbody source. Only by constructing a gradient-doped colloidal quantum dot thermophotovoltaic device were we able to achieve thermophotovoltaic power generation with a power conversion efficiency of 0.39%. The device showed stable operation at ambient temperatures above 100°C.
Acknowledgments

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List of Acronyms

AM1.5G - Air Mass 1.5 Global
AZO - Aluminum doped zinc oxide
BSR - Back side reflector
CQD - Colloidal quantum dot
DFT – Density functional theory
EA - Electron affinity
EDT - Ethanedithiol
EQE - External quantum efficiency
EM - Electromagnetic
FF - Fill factor
FTO - Fluorine doped tin oxide
IQE - Internal quantum efficiency
IR - Infrared
ITO - Indium doped tin oxide
J_sc - Short circuit current density
JV - Current voltage characteristics
KPFM – Kelvin probe force microscopy
MPA - Mercaptopropionic acid
PCE - Power conversion efficiency
PV – Photovoltaic
R_s - Series resistance
R_sh - Shunt resistance
SEM - Scanning electron microscopy
TBAI - Tetrabutylammonium iodide
TPV - Thermophotovoltaic
TCO - Transparent conductive oxide
TiO_2 - Titanium dioxide
TGA - Thermogravimetric analysis
UV - Ultraviolet
V_oc - Open circuit voltage
XPS - X-ray photoelectron spectroscopy
ZnO - Zinc oxide
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1 Introduction

1.1 Motivation

The increasing demand for sustainable energy resources has motivated scientists to pursue the development of a variety of energy conversion technologies. Rising concerns regarding preserving the environment and natural resources has increased the complexity of meeting future energy challenges. Energy efficiency and sustainability are key components of a viable answer to the growing demand for clean energy resources.

In processes in which energy conversion is involved, a portion of power is inevitably lost through heating. Waste heat is thus produced, both from fundamental thermodynamic considerations, and additionally from equipment nonidealities. The resultant heat can be dissipated through parasitic loss mechanisms, including conductive and convective heat, as well as through electromagnetic radiation whose spectral properties are described using Planck’s law.\(^1\) The generated heat reduces the efficiency and functionality of intended primary processes.\(^2\) This thesis therefore concerns the efficient recovery of the waste heat with the goal of overcoming, in part, losses by reinjecting a portion of waste energy back into electrical systems.

Here we present an overview of thermal energy and the main existing conversion strategies. We then introduce the specific topic of thermophotovoltaics, the waste-heat-to-electrical power strategy explored in this thesis, and discuss its major applications and its potential.
1.2 Thermal Energy

In principle, the thermal energy of a system corresponds to its internal kinetic energy and temperature. Different forms of energy can be converted to thermal energy that will be spread out in phase space formed by possible states, increasing temperature.\(^3\)

The conversion of thermal energy into other, higher-value, forms is subject to strict constraints.\(^1,3,4\) Considering the Second Law of Thermodynamics, thermal energy in a system may be converted to other kinds of energy with high efficiencies only if total entropy is increased by other means in a manner that compensates for the decrease in entropy associated with the reduction in thermal energy and its entropy content.

A number of mechanical and electrical approaches have been investigated with the goal of the useful harvest of heat. Heat engines convert (typically very high-temperature, hence high-thermodynamic-quality) thermal energy to mechanical energy. Geothermal and ocean thermal energy conversion systems are major examples of mechanical strategies. Many of these mechanical approaches are aimed at producing electrical power, and are governed by limits described by Carnot’s efficiency.\(^5\)

Additional methods for thermal-to-electronic energy conversion include thermionic, thermoelectric, and thermophotovoltaic methods. Thermionic heat conversion relies on a cold anode as collector and a hot cathode as thermionic emitter. A portion of heat used to extract electrons from the cathode can be
converted into electricity upon collection of electrons by a low-workfunction anode. Thermoelectric strategies use the Seebeck effect to convert a temperature difference into electrical power. Thermophotovoltaic (TPV) techniques, the focus of this work, exploit the photovoltaic effect in a small-bandgap semiconducting medium with the goal of converting emitted heat into electrical power. Each method has its distinct advantages and disadvantages compared to mechanical strategies. They share in common a desirable absence of mechanical moving parts, and therefore increase the potential for durability, scalability, and clean conversion.

1.3 Thermophotovoltaics (TPV)

A portion of excess heat is emitted via radiation of photons. Key features of such radiation, such as the spectral density, power density, and ratio of radiation to total dissipated heat, depend on the distribution in different energy reservoirs, the emissivity of the materials comprising emitters, and the surface morphology and surface-to-volume ratio.

Radiation losses show a fourth power growth with temperature and tend to dominate overall thermal losses at high temperatures. If these radiation losses could instead be used to generate electrical power, this would offer an approach to increase overall system efficiency.

Early work on TPV dates back to the early 1960s, and in recent years the field has shown increased progress and promise. The renewed appeal in TPV has risen mainly due to advancements in small-bandgap photovoltaic material and
device design. New advanced materials and fabrication techniques offer new avenues for the TPV field.

In a TPV energy converting system, thermal energy radiated as photons from emitter is harnessed by a small-bandgap photovoltaic cell and converted to electrical power. A strategy based on the photovoltaic effect provides a one-step energy conversion process and no hazardous byproducts.

Figure 1.1. Schematics of Typical TPV systems.

Thermal energy produced by various sources is absorbed by TPV system. Blackbody radiation from an emitter is harnessed and converted to electricity using a small-bandgap photovoltaic cell. A back side reflector and selective filters provide spectral control of radiation received by the TPV cell. A portion of blackbody radiation that cannot be converted in the PV cell is reflected back to the emitter, returning thermal energy to the emitter to increase its temperature and overall system efficiency as a result.

1.4 Importance and Applications
Benefits of TPV include the potential for high power density; the diversity of fuels and generalized heat sources that can be used towards electricity production; portability and silent operation; operation on demand (as opposed to intermittent operation as with many renewables such as solar and wind); and low maintenance requirements.

TPV can, for example, be used in stand-alone domestic gas furnaces, including by providing cogeneration of electricity and heat; power systems for navigation of sailing boats; silent power supplies on recreational vehicles; and in the large-scale recovery of high-temperature waste heat from industrial processes such as glass manufacture. Military organizations have taken a keen interest in TPV energy conversion because of its strategic benefits. With the recent proliferation of power-hungry mobile devices and microprocessors, significant research efforts have been focused on developing clean, quiet, high-energy-density, and compact chip-scale power thermal-to-electricity converters.

1.5 Thesis Statement

The objective of this thesis is to demonstrate the first solution-processed thermophotovoltaic device. My strategy was to use colloidal quantum dots, materials whose bandgap is tuned in the short- and mid-wave infrared using the size of the nanoparticles. The work, at a device level, involves the realization of a novel gradient-doped structure. To meet this goal, I developed a rational design strategy to overcome challenges and limitations in CQD based infrared photovoltaics. A number of
aspects of the physical and optoelectronic properties of this new class of TPV devices are explored through experimental investigations coupled with theoretical analysis.
2 Background and Literature Review

2.1 Thermophotovoltaics Concepts

TPV systems are composed of an emitter that is thermally coupled to the heat source and radiates photons that are absorbed by a small-bandgap photovoltaic cell. The small-bandgap PV cell is responsible for conversion of emitted radiation. Complementary components such as selective filters in front of the emitter reflecting out-of-band photons can also be implemented. Ancillary components can include power regulation units and a cooling unit to control the temperature of the TPV cell.9,17

The emitter itself is formed using a suitable material, such as tungsten. It is chosen so that it provides high durability at high temperatures, a high ratio of radiation loss to total thermal loss, and the potential to be shaped into the desired geometrical characteristics.17 In some applications, the emitter may be any hot surface, including the working body in a heat engine, the exterior of exhaust pipes in power plants, and melt materials in the recycling industry.

At temperatures specific to the application, the emitter releases the thermal energy through convective, conductive and radiative loss mechanisms. Emitters’ materials and surface morphologies are designed to increase the radiative portion of thermal loss.18
The radiation of heat between the emitter and the photovoltaic cell in a TPV system can be modeled as blackbody radiation at a given emitter temperature.\(^1\)

The spectral radiance of a blackbody source can be described by Planck’s law:

\[
B_\lambda(\lambda, T) = \frac{2hc^2}{\lambda^5 \left( e^{\frac{hc}{\lambda k_B T}} - 1 \right)}
\]

where \(\lambda\) is wavelength, \(T\) represents absolute temperatures, \(k_B\) is Boltzmann’s constant, \(c\) is speed of light, and \(h\) is Planck’s constant. This representation of Planck’s law indicates a characteristic wavelength at which the spectral density peaks. Figure 2.1 shows the spectral radiance and characteristic peaks at different emitter temperatures.

![Spectral radiance and characteristic peaks](image)

**Figure 2.1. Photon emission spectra of blackbody sources at 600, 800, and 1000°C.**

Photon flux densities have been normalized to yield a power density of 50 mW/cm\(^2\) at 800°C.
Typically, the emission peak is located close in the infrared spectral region. It is this that places the focus onto small-bandgap absorber materials in TPV cells. The peak blueshifts as the temperature of the blackbody increases. The radiated power has the following dependence on temperature, and will dominate other loss mechanisms at high temperatures as a result of its strong $T$ dependence:

$$P_{\text{rad}}(T) = \sigma T^4$$

where $P_{\text{rad}}$ is the power radiated by blackbody (which comes from integrating spectral radiance), $T$ is the temperature, and $\sigma$ is the Stefan-Boltzmann constant which in SI units is $5.670367 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$.

This simple model for the spectral distribution of radiated energy plays an important role in the optimization of the photovoltaic medium in a TPV system. The level of accuracy of such modeling depends on the optical coupling factor and spacing, as well as the degree of thermodynamic isolation of the system.

Photons radiated by the emitter are absorbed by the PV medium, where they are subsequently converted into electron-hole pairs. The electrons are extracted into one selective contact, and holes into the other, producing an electrical current.

2.2 Small Bandgap Crystalline TPV Devices
The photovoltaic absorber is at the heart of a TPV cell. Binary, ternary and quaternary alloys of semiconductor crystals such as GaSb, InGaAs, and InGaAsSb have been most extensively explored since they offer a tunable bandgap in the range suited to TPV purposes.\textsuperscript{11,19,20} These semiconducting materials also benefit from maturity of fabrication quality due to years of study and development in the wider optoelectronics sector.

2.2.1 InGaAs and GaSb

Typical crystalline TPV devices share a common structure (Figure 2.2) comprising:

- a front selective filter to provide spectral control

- front contact

- crystalline p-n junction

- back side reflector (BSR)

- substrate; and

- back contact.

Modifications are sought to augment each element of these devices. Spectral control of absorption and reflection of TPV modules has been achieved by integrating optimized selective emitters and filters. With advances in PV materials design and well-matched interfacial layers, the absorption rate of contacts and substrate has been reduced in successive generations of devices.
These improvements have resulted in spectral efficiencies (defined as the ratio of radiated heat absorbed in active region to the total radiated heat absorbed by module) that exceed 80%.\textsuperscript{19–21}

![Typical crystalline TPV device architecture.](image)

**Figure 2.2. Typical crystalline TPV device architecture.**

Thin n-type layers are fabricated on thicker p-type layers to form a p-n junction. Backside filters are made using the same material, but with heavy acceptor doping. Front side filters composed of heavily n-doped material extend spectral selectivity of TPV module as well as facilitating charge extraction.

2.2.2 Performance

Table 2.1 summarizes the main parameters and performance characteristics of crystalline TPV devices. Although 0.53 GaSb cells offer a wider absorption to radiated heat from sources having lower temperatures, the parasitic losses, including substrate absorption, limit spectral efficiency.\textsuperscript{19} Ternary and quaternary alternatives have been sought to replace GaSb.\textsuperscript{20} However, successful matching with substrates complicates the design process and remains an active field of research.\textsuperscript{22}
Table 2.1. Performance results for state-of-the-art crystalline TPV devices under ~1050°C blackbody radiation.\(^a\) (Note: adapted from Reference 21)

<table>
<thead>
<tr>
<th>Device ((\text{In}<em>x\text{Ga}</em>{1-x}\text{As}))</th>
<th>(V_{oc} (V))</th>
<th>(J_{sc} (\text{mA.cm}^{-2}))</th>
<th>(FF) (%)</th>
<th>(\text{Available PCE}^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x=0.68) (0.6 eV)</td>
<td>0.17</td>
<td>9</td>
<td>55</td>
<td>19.1</td>
</tr>
<tr>
<td>(x=0.53) (0.74 eV)</td>
<td>0.22</td>
<td>0.6</td>
<td>57</td>
<td>16.4</td>
</tr>
</tbody>
</table>

\(^a\) J-V results are produced based on a combination of experimental measurements and theoretical calculations by authors.

\(^b\) Available PCE: Power Conversion Efficiency considering only blackbody irradiation above bandgap.

### 2.2.3 Limitations of Prior TPV Cells

Crystalline TPV has yet to gain wide acceptance, a consequence of their high cost. The preparation of materials, and the fabrication of crystalline cells, requires highly equipped facilities as well as costly chemical precursors. The cost per harvest Watt of power is unacceptably high today by orders of magnitude.

In addition to cost, the benefit of conformality also motivates work on flexible TPV cells explored herein. Often the emitter is part of a main system (e.g. an automotive exhaust) and is not planar. It is attractive to develop technologies that can be custom-coupled from emitter to cell, a requirement that demands curved PV cells that are not generally feasible when crystalline substrates are relied upon.

These considerations motivate our focus on low-cost (in both materials and fabrication), physically flexible/shape-adaptable TPV cell technologies.
2.3 Semiconducting Nanocrystals

Colloidal quantum dots are semiconductor materials first synthesized in the late 1980’s, and their synthesis refined in the 1990’s, that have received intensive interest in solar photovoltaics in recent years.\textsuperscript{22} Progress in efficiency has been considerable, and the materials are also starting to mature with respect to fabrication technologies and stability. They are the focus of this thesis.

2.3.1 Solution-Processed Colloidal Quantum Dots

Solution-processed nanocrystals are of particular interest in view of the capacity to tailor their bandgap via the nanoparticles diameter. Their synthesis is relatively facile, being performed at modest temperatures in the solution phase. They can be applied to flexible and curved substrates. In light of their TPV-appropriate bandgap and relative maturity of development, we focus herein on PbS CQDs, the basis of the best CQD solar cells reported to date.\textsuperscript{23,24} Their optical and physical features are now discussed in further detail in light of their particular promise in TPV harvest.

2.3.1.1 Properties and Advantages:

The electronic and physical properties of PbS and PbSe CQDs are precisely controlled during chemical synthesis and materials fabrication process.\textsuperscript{23,25} Researchers have managed to develop a variety of primary or in situ techniques to control properties such as bandgap, electron affinity, charge
carrier density, and spectral absorptance.\textsuperscript{26–29} The size tunability of the CQD bandgap allows for ready control of optical bandgap. Increasing the diameter of these nanocrystals relative to the ~ 3-5 nm range previously studied in depth for solar PV extends the bandgap into the short-wave infrared of interest in TPV applications.\textsuperscript{30,31} Figure 2.3 shows the measured absorbance for PbS CQDs with different diameters and bandgaps suitable for IR PV. Monodispersity of dots is manifest in the IR well-defined excitonic peaks.

\textbf{Figure 2.3. CQD absorption spectra.}
Experimentally measured absorption spectra of colloidal quantum dot solutions having ~ 5, 5.5, and 6 nm average nanoparticle diameters. (These CQDs were synthesized by Dr. Larissa Levina)

The ability to process these nanocrystals from the solution phase facilitates the fabrication of photonic devices. We project that their costs compared very favorably, per square meter of device material, relative to high-vacuum
epitaxy methods such as MBE. CQDs, dispersed as a colloid, can be applied via spin-coating, spray-coating, and dip-coating. These fabrication techniques using relatively simple laboratory equipment with the goal of reducing production cost notably. Significant cost reduction arises from the use of inexpensive source materials and low capital cost.

In addition to the advantages discussed, solution-processed techniques enable the construction of CQD films on curved surfaces. This may be of interest in vehicles and buildings, or in portable and flexible photovoltaic devices, and even wearable photovoltaics. In these TPV applications, the ability to match the device absorber form factor to that of the heat source, with a minimal spacing, offers avenues to enhance optical energy transfer and hence overall system efficiency.

2.3.1.2 Photovoltaic Performance

The performance of CQD PV devices is dominated today by mid-gap energy states, electronic traps that serve as recombination sites. The quality of CQD films used in PV devices strongly depends on the effectiveness of passivation techniques. Device architecture can also be used to help the efficient extraction of photocurrent. Optical matching with the solar spectrum, optical enhancements, efficient dissociation and selective extraction of photogenerated carriers, and band alignment engineering have enabled advances in CQD PV device performance.
Recent advances in passivation techniques and device structure design have led to significant improvements in CQD solar cell performance. Various device structures based on the Schottky junction, depleted heterojunction (DHJ) and quantum junction (QJ) architectures have been investigated. These have employed a range of organic and inorganic ligands and passivation methods.

Among the various device structures, the DHJ is the most attractive to date. Solar cells with DHJ structure have provided the record efficiency of CQD photovoltaics in recent years. Certified PCEs of over 10% were recently achieved under simulated solar illumination (AM1.5 G) conditions. These PbS CQD solar cells incorporated the latest passivation techniques in a DHJ device structure.

2.3.1.3 Longer-Wavelength Infrared PbS CQDs

Larger CQDs for a smaller bandgap may be synthesized for the harvest of TPV infrared photons. Recently, CQDs with bandgaps smaller than 1.3 eV (the 1.3 eV is optimal for single-junction solar cells) were recently used in multi-junction CQD solar cells. In these devices, a CQD layer with a bandgap of 1 eV was used since a 1.6 eV CQD front layer was responsible for harnessing higher-energy photons. Small-bandgap CQDs have been also successfully integrated in a funnel setup aimed at conveying carriers throughout the junction. Nevertheless, relatively few sub-1 eV bandgap
CQD solar cells have been reported. The present represents one of a handful of CQD studies in this spectral regime.\textsuperscript{43} Recently, large PbS CQDs with a first excitonic absorption peak at 1300 nm were successfully employed in modified DHJ PV devices.\textsuperscript{40} These devices can serve as the infrared harnessing unit integrated with silicon or perovskite solar cells, increasing thereby the total PCE of the system.

Nevertheless, for TPV, still lower bandgaps are needed. Here we explore and then overcome the series of obstacles arising from shape change, energy levels, band alignment, transport, and stability that arise as we seek smaller-gap CQD films.\textsuperscript{31} These obstacles created the requirement for significant innovations in this work.

\subsection*{2.3.2 Challenges}

Protocols for chemical synthesis and preparation of CQDs have been initially optimized for solar-optimal-bandgap materials. The surface chemical energy changes considerably when we increase the size of nanocrystals. This imposes new conditions that alter the shape from spherical to cubic. We therefore focus on the synthesis of CQDs with a focus on stability, monodispersity, and the preservation of desirable energy levels.

\subsubsection*{2.3.2.1 Trap States and Surface Passivation}

CQDs in the solution phase are stabilized, forming dispersions with the aid of surface ligands such as oleic acid (OA). These also serve to passivate surface
dangling bonds. Unfortunately, these ligands fail to provide the needed electronic communication between dots. They are therefore replaced with suitable ligands. While these new ligands are intended to passivate dangling bonds too, the disruptive ligand exchange typically leads to an increase in trap states. This limits both minority carrier diffusion length (hence $J_{SC}$) and also quasi-Fermi separation (hence $V_{OC}$). Effective passivation of these trap sites is therefore of crucial importance to achieve a high quality of CQD films.

To date, passivation based on inorganic ligands, particularly tetrabutylammonium iodide (TBAI), and hybrid methods using organic ligands such as MPA, have proven to be the most promising, as judged from device efficiency.

2.3.2.2 Control over Electronic Properties

In the design of optoelectronic devices, band alignment engineering is required for energy levels to match appropriately on either side of an interface. A variety of ligands can be used to control the electronic properties of CQD films. The work function, electron affinity (EA), and carrier density of CQDs can each be tuned via the appropriate choice of ligands. One recent approach involves remote doping of CQDs, while direct application of ligands has been more widely used to control the electronic features of CQD solids.

The electron affinity of CQD films depends on the dominant surface dipoles. A geometrically inhomogeneous charge distribution in the ligand structure,
linked to trenches on the surface of CQDs, will form dipoles. These dipoles may form between ligand and trench, or may include an inner ligand dipole moment as well. Control over this property of CQD films, alongside control over carrier density, provides greater degrees of freedom in aligning bands and the achievement of desired device architectures.

The shape of CQDs changes from a quasi-spherical to a cubic form the dot size is increased to reach smaller bandgaps. This shape change corresponds to faceting of dots wherein they acquire a more favorable total surface energy (Figure 2.4). The appearance of sulfur-rich \{111\} facets, and the inefficiency of passivation by thiol-terminated ligands, makes passivation of these dots a challenging problem.

![Figure 2.4. Comparison of shape and energy levels of small vs. large PbS CQDs.](image)

{111} facets form as the bandgap of CQDs is reduced. This faceting effect exposes sulfur-rich facets on the surfaces of nanocrystals. The bottom panel shows estimated values for energy level differences between 1.3 eV and 0.7 eV CQDs.
Knowledge of the physics of CQDs, especially those having very small bandgaps, is in its early stages. Further studies of the physical properties of small bandgap CQDs could enable advances in the passivation of these large-diameter infrared-bandgap CQDs, and this could help researchers to enhance the quality of IR CQD films used in photonic devices.

2.3.2.3 Absorption

Absorption across the full above-bandgap spectrum is far below unity in all CQD PV devices reported to date. Chemical, physical, and optical techniques have been explored to increase overall absorption of CQD solar cells. The absorption issue remains much more pronounced in smaller-bandgap CQDs near their IR band edge. This puts a serious limit on the spectral efficiency of IR CQD devices.

Increasing the thickness of the CQD layer is accompanied by severe inefficiencies in the extraction of excited photocarriers; the thickness of the active layer today is limited to the sum of drift and diffusion lengths, and, for the moment, extending it further leads to increased recombination and degraded overall performance.

Optical techniques aiming at improving absorption are primarily based on increasing the number of passes that light makes through the active layer. Nanostructured electrodes and intermediate layers such as aluminum-doped zinc oxide (Al:ZnO, AZO) between the back electrode and the CQD active layer are among the most effective strategies investigated to date.
2.3.2.4 Device Structure

Extraction of photogenerated carriers, and improving band alignment, thus remain key challenges in the design of CQD PV devices. Device structure designs for CQD photovoltaics are aimed at incorporating improved charge extraction mechanisms in cells in which proper band alignment between electrodes, CQD layers, and intermediate layers are all optimized. Efforts to date on device engineering have all been tailored to solar bandgap materials.

New constraints arise when TPV cells are pursued. Tuning the PV material and using electrodes that best match the blackbody radiation spectra of objects at temperatures much lower than sun are basic objectives in the design of structures for CQD TPV.

2.3.2.5 Stability

In CQD solar cells, achieving high performance while maintaining stability poses a major challenge. Employing UV curable epoxy to encapsulate devices has been developed with relative success. Ideally, chemical approaches based on ligand engineering will be undertaken. To date, iodide ligands and hybrid passivation offer the best results in stability tests.\(^{37,49}\)

In contrast to 1.3 eV dots used in solar cells, larger-diameter PbS CQDs are subject to the effects of sulfur-rich \{111\} facets. These are exposed due to shape changes and the faceting process. In the absence of protective ligands,
these surfaces are highly prone to oxidation and the formation of PbSO₄ associated with deep traps.⁴⁰,⁵⁰

The thermal stability of PV devices is also important, particularly in TPV applications in which the operating temperature of devices can be much higher than in the case of solar cells. Cooling methods to reduce device temperature can be used to preserve materials and interface quality and maintain maximal efficiency; however, complex cooling methods that seek to keep devices below 100°C would likely add undue cost.

2.4 Optimization Constraints

Radiative recombination is the fundamental loss mechanism in ideal single-junction photovoltaics; it cannot be avoided since it is the time-reversed process of absorption. Fundamental efficiency limits are imposed by a detailed balance principle, and these allow us to determine maximum efficiencies and optimal bandgaps. This is the basis of the detailed balance analysis of Shockley and Queisser.⁵¹

We established our model based on a single-junction cell operating at room temperature. Initially we consider a tunable bandgap and allow for (best-case) radiative recombination only. This PV cell absorbs blackbody radiation from an ideal wide-band blackbody emitter operating at controllable temperatures relevant to most TPV applications. The solid angle chosen for the blackbody emitter is chosen to be π, corresponding to the case of minimum spacing between emitter and absorber. The geometrical configuration, specifically the
small distance between emitter and PV cell, functions analogously to light concentration in solar PV. The maximum efficiency limit in TPV systems is high as a result: Figure 2.5 shows the detailed balance limit of PCE at different source temperatures. The optimal bandgap associated with maximum efficiency is plotted as a function of source temperature. This model yields a limit of 44% efficiency at 6000 K (close to the sun’s temperature), consistent with the Shockley-Queisser at full concentration.

![Figure 2.5](image_url)

**Figure 2.5. Thermodynamic detailed balance analysis for broadband TPV devices.**
Calculated ideal-case (100% absorption) overall power conversion efficiency (red curves) of optimal-bandgap (blue curves) TPV cells engineered for 600, 800, and 1000 °C blackbody sources at an absorber temperature of or 27 °C (solid) or 100 °C (dashed).
Further modifications and practical loss mechanisms can be added to the Shockley-Queisser model to approach the conditions of practical PV cells. Reflection and absorption losses in the front electrode and auxiliary layers, non-radiative recombination processes such as Auger recombination, parasitic losses, real absorption spectra of CQD films, can all be taken into account.

As shown in Figure 2.5, the detailed balance limit analysis indicates an optimal bandgap near 0.3 eV for the harvest of emission from an 800°C blackbody source. TPV devices can be combined with a shortpass filter that passes higher-energy photons to an efficient photovoltaic device and reflects lower-energy photons to raise the temperature of the hot body.

We focused therefore on CQDs having $E_g \sim 0.75$ eV. Developing a TPV device based on these materials would represent a record in efficient and stable harvesting of low-energy photons while taking advantage of a photon energy of which these materials were practically capable. Quantum dots having diameters in the range ~ 5.5 to 6 nm use synthesis processes described previously in published protocols.$^{37,49,52}$ The resulting materials exhibited a high degree of monodispersity, evidenced by the well-defined exciton absorption peak (Figure 2.3).

2.5 Conclusion

This chapter introduced the requirements for the realization of efficient TPV devices. We also pointed out challenges associated with prior generations of devices, especially the high cost of epitaxy. We then turned our attention to
low-cost, manufacturable, size-tuned CQD TPV. We identified the specific challenges – notably absorption, transport, and band alignment – to translating solar CQD PV into the TPV domain. In the chapter that follows, we will apply this context to devise the first TPV devices based on IR CQDs.
3 Device Architecture: Initial Attempts

Efficient extraction of photogenerated carriers in quantum dot films requires device structures in which proper band alignment between different layers provides the means for carrier transport and extraction. Although vast research has been carried out on different structure designs for CQD solar cells,\textsuperscript{24,25} little has been done regarding device structures optimized for TPV purposes.

Widely used structures are the best starting points for our TPV device design. In this chapter, first we briefly discuss the best CQD PV device architectures. We then present our results on the fabrication of large-dot versions of these devices. Analyzing the results of these experiments helps us gain insight into key factors in the design of our solution-processed TPV devices.

3.1 Frequently-Used CQD Device Structures

The Schottky junction structure was used in the first CQD solar cells and provided PCEs exceeding 1%.\textsuperscript{53} In this structure, the CQD active layer is sandwiched between a deep work function transparent conductive oxide (TCO) such as ITO, and a metal electrode such as aluminum or magnesium on the back side of the device. The charge separation mechanism is based on a Schottky junction created between the CQD active layer and the back electrode, while the other electrode forms an ohmic contact. Internal quantum efficiencies (IQE) of higher than 80% and PCEs of up to 4.6% have been achieved using different variants of this structure.\textsuperscript{39,53}
In a Schottky structure, the built-in field enhances charge separation and transport in the depletion region. However, the thickness of the depletion region is limited in this junction, and outside of this region, the transport of minority carriers relies on diffusion. This, in turn, is limited by recombinative trap states in the quasi-neutral region.\textsuperscript{32,54} The thickness of the active layer is limited as a result, and cannot be increased to provide near-complete absorption.

Moreover, the Schottky junction responsible for exciton dissociation is formed at the back side of the active layer, whereas the majority of photons are absorbed on the front side of the active layer. There exist no selective energy barriers that would prevent the extraction of holes that diffuse to the front contact. Although significant improvements in the electronic properties of CQD films and the diffusion length of photogenerated carriers have resulted in improved conversion efficiencies, still these limitations led researchers to investigate alternative structures for CQD photovoltaic devices.

In 2010, a CQD solar cell structure was introduced that was based on diffusive exciton transport. It employed a large-bandgap transparent conductive oxide such as TiO\textsubscript{2}, or ZnO.\textsuperscript{37} This produced a depleted heterojunction with the CQD film.\textsuperscript{32} The significant difference between free carrier densities of TCO and CQD film creates a depletion region in the front region of the active layer. The large-bandgap TCO blocks unwanted extraction of holes that diffuse to the front electrode. A variety of modifications have led to PCEs of 7\% for TiO\textsubscript{2} and 9\% for ZnO.\textsuperscript{28,35}
ZnO and TiO₂ are the most successful and widely-used large-bandgap TCO materials in the DHJ device structure. They have electron affinities of near 4.1 eV (depending on fabrication conditions and controlling parameters) and bandgaps of near 3.2 eV, and they behave as n-type materials. These transparent oxides offer a viable option for DHJ devices based on ~1.3 eV CQDs with a LUMO near -3.8 eV.³²,³⁵

Unfortunately, the DHJ device structure suffers from a limitation: its sensitivity to band alignment at the TCO/CQD type II heterointerface. A proper band alignment requires that the energy offset between TCO and CQDs be sufficient to prevent hole extraction, and at the same time support electron extraction; yet the latter offset cannot be so large as to limit \( V_{oc} \), or negative such as to block electrons. This necessitates tailoring of the TCO when the CQD bandgap or the ligands are adjusted.

In 2012, a CQD PV device structure was introduced based on the formation of a quantum dot-based junction between CQD solids having the same bandgap but different doping type.³⁶ Since the rectifying junction is formed between two similar quantum dot solids, the quantum junction device is less prone to size-tuned changes in band offsets. The best published quantum junction PV device consists of an ITO substrate as the front electrode forming an ohmic contact with active layer; a thin PbS CQD layer treated with TMAOH serves as the p-side of the junction, while TBAI-treated PbS CQDs on top form the n-type layer. A thin layer of aluminum doped zinc oxide (AZO) is deposited
onto the CQD active layer before deposition of the top silver top electrode. The AZO/silver layer also plays the role of a back-side reflector.\textsuperscript{48}

3.2 Initial Attempts

We began our efforts towards TPV devices by replacing conventional CQDs having a first exciton peak at \(~900\) nm with infrared CQDs with their first exciton peak at \(~1700\) nm. We fabricated variety of devices using the best published device structures for photovoltaics discussed earlier.

3.2.1 Depleted Heterojunction

We fabricated a suite of devices employing PbS CQDs with first excitonic peaks at \(~1700\) nm, attempting fabrication both on TiO\textsubscript{2} and on ZnO layers. Performance was very poor: Figure 3.1 shows the current-voltage (J-V) characteristics of these devices, and the performance parameters are summarized in Table 3.1.

We found that the problem originated from a barrier to electron extraction arising from energy misalignment between CQDs and the TCO layer: as the size of dots is increased, the reduction in their bandgap mainly lowers LUMO level, as illustrated in Figure 2.4. The LUMO level is then so deep that an energy spike appears in the interface. The resulting energy barrier prevents photogenerated electrons from being extracted; instead, they accumulate and recombine on the CQD side of the energy spike.
Figure 3.1. Depleted Heterojunction and Quantum Junction TPV Device Attempts.

Experimentally-measured current-voltage curves. All devices were illuminated using broadband infrared light from an 800 °C blackbody. The intensity incident on the device was 52 mW/cm² in each case. DHJ solar cells were based on 0.75 eV quantum dots and included both ZnO electrode (blue) and TiO² electrode (red). Also shown are quantum junction solar cells based on 0.75 eV quantum dots with an active layer thickness of 250 nm (green) and 350 nm (violet). 250 nm was found to be the optimal thickness; using a thicker active layer decreases performance, which implies the lack of an effective drift force.

Table 3.1. Performance results for different architectures under 800 °C blackbody radiation.⁹

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA.cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Available PCE b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHJ (TiO₂)</td>
<td>0.15</td>
<td>0.21</td>
<td>12</td>
<td>&lt; 0.01</td>
<td>-</td>
</tr>
<tr>
<td>BHJ (ZnO)</td>
<td>0.19</td>
<td>0.26</td>
<td>14</td>
<td>&lt; 0.01</td>
<td>-</td>
</tr>
<tr>
<td>QJ (250 nm)</td>
<td>0.19</td>
<td>0.72</td>
<td>35</td>
<td>0.09</td>
<td>1.6</td>
</tr>
<tr>
<td>QJ (350 nm)</td>
<td>0.17</td>
<td>0.83</td>
<td>26</td>
<td>0.07</td>
<td>1.3</td>
</tr>
</tbody>
</table>

⁹ J-V measurements has been done using a blackbody at ~800°C with a power density of 52.2 mW.cm².

b Available PCE: Power Conversion Efficiency considering only blackbody irradiation above bandgap.
Figure 3.2. One dimensional self-consistent optoelectronic simulations.
Band misalignment between large PbS CQDs and TiO$_2$ or ZnO is illustrated. An energy spike and misalignment at the interface prevents extraction of photogenerated electrons.

Altering the electron affinity of the TCO and CQD layers can help to produce the desired energy alignment between them. We tried lowering the conducting band of TCO by investigating antimony (Sb) treatment for TiO$_2$ and iodine treatment for ZnO. However, none of these approaches successfully removed the large energy barrier in the interface.

As previously discussed, several ligands have been reported to change energy levels of PbS QDs considerable. Thus, we attempted different ligands such as TMAOH, TPT, and MPA, either as a replacement or an addition to TBAI treatment, with the goal of increasing the LUMO level of the CQDs (Figure 3.3). The dependence of the work function on ligand concentration in TBAI and MPA-treated PbS CQDs can be seen in Figure 3.4. Fermi levels have been measured using Kelvin probe force microscopy (KPFM). Although significant control over the energy levels of 0.75 eV PbS CQDs was achieved by mixing different ligands with different concentrations, the increase in LUMO level
was still insufficient to allow the proper alignment. This prevented the DHJ structure from enabling the full potential of size-tuned CQDs for TPV purposes.

Figure 3.3. Relative energy levels of differently-treated PbS CQDs.
As measured using KPFM, p-type MPA treated CQD film has a work function of 5.3 eV while n-type TBAI treated CQD film has work function of 5.1 eV. Work function and band edges of MPA-TBAI co-doped CQD solids reside, as expected, part-way between those of the MPA and TBAI primitives.
Figure 3.4. Fermi levels for different ligand concentrations as measured by Kelvin probe force microscopy.

(a) Increasing MPA concentration from 1% to 5% and 10% resulted in slightly larger work functions. However, increasing MPA concentration above 10% led to smaller work functions. Since MPA treated films behave as p-type semiconductor, the small increase in Fermi level suggests a higher LUMO and smaller absolute value for EA as desired. Unfortunately, increasing either MPA concentration to values higher than 20% proved to be clearly damaging film quality significantly. (b) Deeper Fermi level at higher concentration of TBAI treatment on CQD films.

3.2.2 Quantum Junction

Next, we turned our focus to quantum junction (QJ), a junction between two quantum dot solids that is less prone to size-tuned changes in band offsets. We began by deploying the previously-published TMAOH-treated CQD layer
on the p-side, and TBAI-treated PbS CQD layer on the n-type side.

Unfortunately, again we obtained poor performance. When we varied the thickness of active layer, we found that the optimal choice is approximately 250 nm (Table 3.2), with thicker devices showing lower performance, indicating carrier-transport-limited current.

Table 3.2. Performance results for different thicknesses of active layer in QJ devices using 0.7 eV CQDs under 800 °C blackbody radiation.

<table>
<thead>
<tr>
<th>Thickness of Active Layer</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA.cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Available PCE $^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QJ (180 nm)</td>
<td>0.19</td>
<td>0.63</td>
<td>37</td>
<td>0.09</td>
<td>1.5</td>
</tr>
<tr>
<td>QJ (250 nm)</td>
<td>0.19</td>
<td>0.72</td>
<td>35</td>
<td>0.09</td>
<td>1.6</td>
</tr>
<tr>
<td>QJ (300 nm)</td>
<td>0.18</td>
<td>0.79</td>
<td>31</td>
<td>0.08</td>
<td>1.5</td>
</tr>
<tr>
<td>QJ (350 nm)</td>
<td>0.18</td>
<td>0.83</td>
<td>26</td>
<td>0.07</td>
<td>1.3</td>
</tr>
</tbody>
</table>

$^a$ J-V measurements has been done using a blackbody at ~800 °C with a power density of 52.2 mW.cm$^{-2}$.

$^b$ Available PCE: Power Conversion Efficiency considering only blackbody irradiation above bandgap.

1D self-consistent optoelectronic simulations confirmed intuition regarding origins of poor performance of this device. Figure 3.5 shows the band alignment and transport failure when the thickness of the active layer exceeds that of the optimal case. We conclude that the depletion region was insufficiently wide to achieve charge collection over the length scales needed to absorb an appreciable fraction of incident IR photons.
Figure 3.5. 1D self-consistent optoelectronic simulations of small-bandgap QJ devices.
The lack of a sufficiently wide depletion range limits the collection of an appreciable fraction of photogenerated carriers given that the absorption length is above 500 nm near the 1.7 um CQD bandgap.

3.3 Conclusion

By employing a thermodynamic model based on detailed balance considerations, as well as material and fabrication concerns, we estimated the theoretical efficiency limits for optimal bandgaps as a function of blackbody temperature. Optimal bandgaps of below 0.8 eV required for TPV could not match properly with available TCO materials in the DHJ structure. We focused therefore onto the quantum junction approach with the goal of exploiting size-tunability.

However, low absorptance of infrared photons over the available thickness of active layer, together with limited depletion region and diffusion lengths, resulted in poor performance of quantum junction TPV devices. We therefore sought in the next chapter a strategy that would overcome these issues.
4 Gradient-Doped TPV Devices

In principle, enhancing carrier transport by creating a wide drift region across the active CQD layer should allow for the extraction of photogenerated carriers over a larger lengthscale. Such a drift force can be achieved by implementing a spatial gradient in the electron affinity and carrier densities. Here, we begin by studying the role of gradients in energy levels. We then proceed to describe our approach, wherein we employ the diffusion of iodine anions and discuss the parameters that control this process. Finally, we present the optimization of this gradient-doped TPV device structure.

4.1 Graded Electron Affinity and Carrier Density

According to self-consistent 1D optoelectronic modeling, a gradient in energy levels of active layer can be achieved by grading electron affinity and minority carrier concentration along the active layer thickness dimension (Figure 4.1 and 4.2). We studied a number of grading profiles. The precise values of carrier densities in halide-treated large dots are not known, so we focused on ranges for EA and carrier densities.

Simulation results clearly show that a gradient in energy levels improves photogenerated current by producing enhanced field-driven charge transport (Figure 4.2).
Figure 4.1. Band alignment and charge transport process in gradient-doped CQD TPV device.

1D self-consistent optoelectronic simulations predict a spatial band diagram offering effective force fields over a notably more extended thickness. Iodide anions diffuse into the bottom p-layer forming a gradient in carrier density and EA of active layer.
Figure 4.2. Effect of gradient-doped active layer.

1-D optoelectronic modeling and simulations of 0.7 eV PbS CQD devices with and without gradient-doping subjected to 1000°C blackbody radiation with an incident power density of 100 mW cm−2. Energy band diagrams of junctions with no EA offset between p and n layers and no gradient-doping (a), with a 0.25 eV EA offset and no gradient-doping (b), and with 0.25 eV EA offset exploited for gradient-doping (c). Panel (d) compares simulated J-V characteristics of the junctions. The increase in $V_{MPP}$ and $J_{MPP}$ is mainly due to increase in absorption and enhanced field-driven carrier transport. Optimal thickness of n-layer in device models with and without gradient-doping has been also estimated (e). Simulations show near 100 nm increase in optimal thickness range for gradient-doped devices.

In addition, simulations confirm that the difference in EA on the n- and p-type sides of the junction sets a limit on how extended the graded junction can become. Based on an optoelectronic device model, an energy offset of -0.2 eV
between p-type and n-type layers is the lower limit, and is expected to cancel out Fermi separation; where an offset of 0.5 eV is the upper limit imposed by fabrication feasibility. Theoretical estimations show that offset values of approximately 0.25 eV can satisfy energy requirements for desired iodine diffusion.

4.2 Implementation of a Graded Doping Profile

During our investigation into the role of ligands in altering the electron affinity of CQD films, we observed that iodine anions migrate from TBAI treated layer into the adjacent CQD layer that had experienced different treatments. Such diffusion processes change the profile of iodine concentration, providing a means to control energy levels throughout the CQD active layer.

4.2.1 Iodine Diffusion

We hypothesized that, since iodide is known to diffuse over appreciable distances, we could take advantage of this effect to produce a gradient in iodide concentration, hence in electron affinity and carrier densities (Figure 4.1 and 4.3). However, there are certain energy and spatial requirements necessary for effective diffusion of iodine anions from PbS-TBAI layer into host CQD layer.
First, the host CQD layer needs to have an electron affinity smaller than TBAI treated layer in order to allow formation of a proper gradient. For small differences in EA of CQD layers, iodine diffusion occurs at much smaller scales, resulting merely in a smooth gradient in energy and a weak built-in field.

In addition, increasing the space available for iodine diffusion (i.e. the thickness of the host layer) escalates migration of diffusive iodine anions into the host layer. Thus, controlling the bottom p-layer thickness could provide the means by which we could control the spatial extent of gradient in electron affinity and carrier density. This could lead to the desired graded energy profile.
4.2.2 Ligands

Satisfying the energy requirements for the formation of an effective gradient demands replacing TMAOH treatment with an alternative ligand that provides more positive surface dipoles.\(^{44}\) In addition, such alternative ligand needs to passivate the trap states effectively on the CQD surface. Furthermore, the stability of the CQD film, as well as chemical compatibility with other materials such as iodine, is an important concern.

MPA is an organic ligand proven to provide good passivation of deep electronic trap states, as well as crosslinking the dots in CQD solid effectively.\(^{55}\)

Offering a significantly shallower LUMO compared to TBAI and TMAOH, MPA treatment is also compatible with other materials in the TPV device, specifically ITO and TBAI. Figure 4.4 shows result of DFT simulations comparing effect of MPA, TMAOH and TBAI.
Figure 4.4. Simulated DOS for PbS CQDs with MPA, TMAOH, and TBAI treatments. DFT simulations show that MPA treated CQDs have shallower bandedges as compared to TMAOH and TBAI treated CQDs. (Simulations provided by Dr. Oleksandr Voznyy)

We therefore concentrated our focus on the optimization of different parts of the device based on an active layer consisting of PbS-MPA as the host layer beneath the PbS-TBAI layer.
4.3 Device Optimization

Several devices were fabricated by varying device parameters that included the ligand concentration used in treatment, the thickness of PbS-TBAI layer, the thickness of PbS-MPA layer and consequently the gradient in iodine concentration profile.

4.3.1 Ligand Concentrations

We expected that larger PbS CQDs would need a less aggressive treatment compared to ~1.3 eV PbS CQDs for which the treatment process had originally been optimized. The main reason for this difference is the shape change and faceting as the size of dots is increased. The surfaces on large dots make them vulnerable to aggressive treatments widely used. Thus, we first reduced the duration and intensity of treatment processes until an optimal ligand exchange process was achieved. Details are presented in the appendix titled Methods.

4.3.2 Thickness of Layers

We then tracked changes in device performance parameters and analyzed sputtering XPS results, seeking to find an optimal thickness and concentration by varying the number of spin-cast layers treated with MPA and TBAI while using different ligand concentrations in the discussed range. Optimal thicknesses of near 150 nm for the PbS-MPA layer and 350 nm for the PbS-
TBAI layer were obtained in this manner. The complete device structure and cross-sectional SEM image are presented in Figure 4.4 and 4.5.

Figure 4.5. Schematics of gradient-doped devices.

Figure 4.6. Cross-sectional SEM of device.
4.4 Conclusion

By exploiting iodine diffusion to implement the proper gradient in energy levels of the active layer, we were able to develop a TPV device structure that provides efficient extraction of photocarriers over a wide region. Such gradient-doped structure was expected to offer superior performance under blackbody radiation as predicted by device modeling and 1D optoelectronic simulations.

We proceeded by fabricating TPV devices based on ~ 0.7 eV CQDs in the gradient-doped structure. Further optimization of device parameters including thickness and ligand concentration of different layers was carried out in fabrication process to achieve best efficiency. Next, we performed a thorough performance analysis of efficiency and stability as discussed in the next chapter.

5 Device Characterization and Performance Analysis

As discussed in the previous chapter, the implemented gradient in electron affinity and energy levels of the active layer plays a crucial role in yielding an efficient, stable CQD TPV device. In this chapter, we present the thermophotovoltaic performance of the device in conversion efficiencies at different blackbody temperatures. We also provide a spectral study of quantum efficiencies. Finally, temporal and thermal stability studies are presented.
5.1 Performance Analysis

5.1.1 Current-Voltage Characterization

A blackbody radiation and device characterization setup was designed to simulate operating conditions in TPV applications. The main blackbody emitter was a tungsten-halogen lamp set to temperatures near 800°C, as indicated by the spectral profile of the emission. The glass bulb was placed 1 cm from the TPV cell. The radiation power density received by the cell was measured to be 52.2 mW/cm\(^2\) distributed over a spectrum between 200 nm to 20 µm. This blackbody radiator and measurement setup were used for conversion efficiency measurements.

The full device exhibited an excellent rectification ratio in excess of 1000 in numerous samples. The current-voltage performance under illumination using blackbody radiation (800°C, 52 mW/cm\(^2\)) is shown in Figure 5.1. The device achieved an overall power conversion efficiency of 0.39%: this corresponds to a generated electrical power density of 0.20 mW/cm\(^2\) under illumination by the 800°C blackbody source (Table 5.1).
Figure 5.1. Experimentally-Measured Current-Voltage Curves.

All devices were illuminated using broadband infrared light from an 800°C blackbody and the intensity incident on the device was 52 mW/cm². Experimentally-measured current-voltage curves for the TPV device studied herein (black). J-V characteristics of initial attempts on DHJ and QJ structures are also included for comparison.

Table 5.1. Performance parameters of gradient-doped TPV device.a

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA.cm⁻²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Available PCE b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gradient-doped</td>
<td>0.21</td>
<td>3.1</td>
<td>32</td>
<td>0.39</td>
<td>6.8</td>
</tr>
</tbody>
</table>

a J-V measurements has been done using a blackbody at ~800 °C with a power density of 52.2 mW.cm⁻².
b Available PCE: Power Conversion Efficiency considering only blackbody irradiation above bandgap.

Since TPV devices can be constructed that reflect sub-gap illumination to the source,¹⁸,²¹,⁵⁶ their power efficiency can also meaningfully be reported based on the power in the blackbody spectrum that resides above the absorber’s bandgap. This analysis for a 0.75 eV cutoff bandgap produces a value of 6.8%
(blackbody temperature ~800°C) compared to an analogous figure of 19% for an epitaxial InGaAs TPV device (blackbody temperature ~1030°C).

5.1.2 Quantum Efficiency

The external quantum efficiency spectrum in Figure 5.2 shows that electrons generated by the absorption of high-energy photons close to the front electrode are too far from the electron-accepting AZO electrode to be collected efficiently. In contrast, a significant fraction of low-energy photons are absorbed deeper in the active layer. In this case, photogenerated electrons are not required to transit through a p-type layer before they reach the back contact, and their recombination losses are much lower as a result.

**Figure 5.2. Measured external quantum efficiency.**
Despite the loss of EQE in lower wavelengths, devices show enhanced EQE in the relevant 1500-1800 nm region.
5.2 Stability

One of the key challenges for energy-converting devices and materials, and specifically for CQD devices, is to achieve stability of performance under operating conditions. Thermal stability is therefore important since the TPV cell is ideally very close to the heat source.

5.2.1 Temporal Stability

Larger quantum dots are generally more prone to oxidation and its effects on trap states, transport and device performance. To better preserve devices from air exposure, we encapsulated samples using a UV cured epoxy (Methods). After encapsulating devices with a thin heat sink bonded with thermally conductive epoxy, only near 20% of performance was lost over a course of more than 10 days of storage in air at 100°C (Figure 5.4). There was an initial settling of performance as a function of storage days, a fact due to bake-out of the encapsulant. This effect is excluded from the temporal stability analysis (it is treated as an initial burn-in effect that is part of final device processing).
5.2.2 Thermal Stability

An ideal TPV device will be immune to temperature cycling. To measure the behavior of devices after temperature cycling, samples are heated to 100°C for 1 minute, cooled down to room temperature, measured, and again the cycle is repeated. Results of temperature cycling experiment are demonstrated in Figure 5.5. After repeating the cycle more than 20 times, there is little loss in device performance.
Figure 5.4. Thermal stability studies.
(a) The relative power output of the device of Figure 3d, studied as a function of thermal cycling. (b) The relative power output of the same device, studied as a function of annealing temperature. The device fails at temperatures higher than 140 °C.

The thermal stability of devices is also studied with respect to the failure temperature, i.e. the temperature after which the performance is permanently lost. We show in Figure 5.5.b the PCE after the devices are annealed for 10 minutes at increasing temperatures. Devices maintain 80 percent of their performance after being annealed at temperatures up to 140°C.
5.2.3 Origins

We also sought to investigate the thermal stability of the CQD films. Widely used ligands that render CQDs to be conductive inside a solid film as well as provide surface passivation are based on organic molecules. Unlike halide ligands, the bond of an organic ligand onto an inorganic surface tends to be unstable at elevated temperatures, which is unfavorable for TPV applications.

We compare the thermal stability of the two types of passivation by thermogravimetric analysis (TGA) and GC-MS measurements (Figure 5.7). Up to 200°C, both the organic and inorganic ligand containing materials lose the same amount of mass, which likely corresponds to left-over solvents. Beyond 200°C there is a stark difference in thermal stability, with the inorganically-passivated quantum dots only gradually losing mass, compared to the sudden mass-loss associated with the loss of the organic ligands.
Figure 5.5. Thermogravimetric analysis of MPA and TBAI PbS CQD solids.

Primary smooth loss of mass is mainly associated with losing left over solvents. Drastic loss of mass in MPA sample (red), as opposed to TBAI sample (blue), which starts before 200°C indicates desorbed MPA fragments.

(Measurements were carried out in collaboration with Dr. Jeffrey McDowell)

In the most likely scenario, a reaction occurs due to high temperature annealing, and this generates the Pb-SH structures on the surface of dots that are highly sensitive to oxidation. Higher temperatures may increase the density of Pb-SH, and its oxidation will lead to excessive surface traps in the MPA-treated samples. These new traps may be caused by the oxidation of Pb-SH, and they will make $V_{OC}$ and especially $J_{SC}$ drop dramatically compared to the TBAI samples in which oxidation is suppressed.

5.3 Conclusion

In this chapter we determined the key performance-relevant parameters of the new solution-processed TPV device that is the heart of this thesis. We found
that the gradient-doped device provided major advantages over relevant controls based on traditional prior architectures and materials processing strategies. The graded device achieved more efficient transport processes, as confirmed using spectral quantum efficiency analysis.

This chapter also included initial studies of temporal and thermal stability. The gradient-doped device exhibits superior stability including in the TPV operating regime.
6 Conclusions

6.1 Review of Thesis Objectives and Their Achievement

This thesis began with the proposal that it would be attractive to design and create a low-cost thermophotovoltaic device. We reasoned that a rational design strategy could enable large-scale, low-cost devices that could be conformed to a curved surface such as an exhaust pipe. This goal was met through the first report of solution-processed thermophotovoltaic devices reported herein. The approach was based on PbS CQDs in light of their combined solution-processing and their size-effect tuning into relevant short-wavelength infrared spectral regimes. The findings reported herein, including the means of achieving enhanced performance via gradient doping and the resultant enhanced stability, offer further avenues to investigate and optimize solution-processed thermophotovoltaics and infrared power conversion (detailed in 6.3 below).

6.2 Contributions to the Field

The main finding herein that a gradient-doped TPV device based on CQDs offers significant performance and robustness advantage can be broken down into these specific contributions:

- It represented the first design and fabrication of a solution-processed TPV device;
• It provided a new class of CQD photovoltaic devices that leverage gradient doping and effective force field;

• It exploited the diffusion of halide dopants to provide the doping gradient;

• It addressed the problem of thermal stability of prior IR CQD materials;

• It provided a solution to the problem of the mismatch between small-gap CQD solids and available electron-accepting electrodes;

• It led to the development of an enhanced physical device model that could be further extended in future related studies.

6.3 Future Directions

One important avenue for TPV is to extend the bandgap to even longer spectral regimes to enable TPV at lower hot body temperatures.

Unfortunately, large-diameter small-bandgap CQDs are far from maturity in their quality. Deeper investigation of these materials – such as studies of how greater faceting on higher-diameter dots leads to higher trap state densities – will be crucial to achieving further improvements. Understanding and overcoming issues such as inferior minority carrier diffusion lengths in small-gap CQD solids will enable notable enhancement once the trap density issue is addressed. This will likely rely on new passivation strategies to control the energy properties of the active layer.
Various materials and compounds can be investigated as candidates for the TPV absorber. Hg$_{1-x}$Cd$_x$Te (MCT) is an appealing PV material to harness long wavelength blackbody radiation. Its bandgap is tunable from ~ 0 eV (i.e. semimetal HgTe) to ~ 1.5 eV (i.e. CdTe), as a result of which MCT’s absorption spectrum can be matched well with the emission spectra of low temperature blackbody radiators. This material can provide electron mobility values higher than most direct bandgap PV materials except GaSb and InGaAs compounds. To date, MCT has mainly been exploited in IR photodetection.$^{57}$ However, the low thermal conductivity of MCT, especially at high mercury content, poses challenges in applications including TPV.

New nanocrystal designs such as ternary and quaternary CQDs (e.g. HgCdTe nanocrystals) can also offer an interesting path in the direction of advancing PV materials. To date, research on CQD materials has been focused on binary nanocrystals, with fewer studies on ternary or quaternary compounds reported.$^{58}$ In principle, new surface structures on such nanocrystals can provide the opportunity to gain better control over surface properties, potentially enabling improved stability and enhanced transport properties in networks of CQDs.

The spectral efficiency of TPV devices also requires further advances such as using optical strategies. A nanostructured back mirror provides one encouraging avenue: absorption in the active layer can be enhanced by scattering, instead of specularly reflecting, light that reaches the back surface of the device. The high index of the active layer can then be exploited to
overcome transport limitations. One recent successful approach developed for CQD devices exploits nanoscale pyramids as light-trapping centers, increasing absorption by increasing the number of passes for photons in the active layer. Alongside the benefits of solution-processability, this approach can offer up to a 50% enhancement in the photocurrent of CQD solar cells. This translates to a near-30% expected increase in PCE in light of a modest compromise to voltage. In our TPV devices, straightforward calculations for increasing $J_{SC}$ while accounting for the decrease in $V_{OC}$ and FF indicate that over 20% in PCE enhancement can be expected.

In numerous applications, a CQD-based TPV cell can be integrated with other energy systems to improve further the system efficiency. Here an optimized front side reflector can also be included to reflect high-energy photons. These photons will be available to maximize the temperature of the hot body while not suffering thermal losses in the TPV device.

Spectrally-selective emitters and filters comprised of rare-salt materials such as Yb$_2$O$_3$ can be used to optimize further the spectral matching of emission with the properties of cell. An estimate based on IQE and absorption spectra of our TPV devices indicates that the present-day spectral efficiency of ~50% can be improved up to 87%. This could provide a notable increase of near 70% in PCE.

Exploitation of new and distinct PV mechanisms can also be contemplated. These include the use of intersubband transitions in a nanostructured quantum
cascade (QC) architecture, an approach that can offer paths to harnessing very long-wavelength radiations.\textsuperscript{59} Such structures have been mainly exploited in quantum cascade long-wavelength photodetectors, and are yet to be fully explored in thermophotovoltaics.\textsuperscript{60} The QC principle has been widely investigated in crystalline (epitaxial) devices; there exists considerable room to explore this phenomenon in CQD-based materials and devices.\textsuperscript{61}
7 Appendices

7.1 CQD Preparation and Device Fabrication

PbS CQDs were synthesized by Dr. Larissa Levina using a variation on a literature method.\textsuperscript{52}

Absorbance Measurements:

We used a Cary 500 UV-Vis-IR spectrophotometer for optical absorption measurements. The absorbance is measured using an integrating sphere and at normal incidence.

CQD film and Device Fabrication

Quantum dot films were prepared using multilayer spincoating of 40 mg mL\textsuperscript{-1} solution in a 3:1 mixture of octane:decane under ambient conditions. Each layer was deposited at 2500 rpm and treated briefly with 10 vol % 3-mercaptobutryonic acid in methanol also spin-cast at 2500 rpm; each layer was then rinsed with methanol and octane while spinning at 2500 rpm. Next, PbS CQDs were spin-cast at the same speed but with 7-10 mg/mL TBAI treatment and 5 seconds of soaking time. Spincoating was carried out in air for all layers. The device was then transferred to a glovebox with N\textsubscript{2} atmosphere and left overnight. The ohmic contacts were the ITO substrate for the MPA-treated p-type quantum dots and sputtered Al:ZnO (AZO) for the n-type quantum dots. Finally, silver contacts, 60 nm thick, were deposited by
thermal evaporation at a rate of 0.4 Å/s at a pressure of <1 × 10⁻⁶ mbar.

Contact sizes were 0.1667 cm².

7.2 Device Characterization

Performance Measurements:

We designed a TPV system composed of tungsten-halogen lamps as blackbody emitter, TPV cells, heat sink accessories, and employed a Keithley measurement system for all current-voltage studies. A glass bulb was placed 1 cm from the TPV cell. The radiation power density received by the cell was measured to be 52 mW/cm² distributed over a spectrum between 200 nm to 20 µm. J-V data were acquired using a Keithley 2400 source-meter. Devices were encapsulated using UV curing epoxy. The source intensity was measured with a Melles-Griot broadband power meter (responsive from 200 to 20 µm without filter), through a circular 0.1667 cm² aperture at the position of the sample. The accuracy of the power measurements was estimated to be ±7%. 
External Quantum Efficiency Spectra:

External quantum efficiency spectra were obtained by passing the output of a 450 W Xenon lamp through a monochromator and using appropriate order-sorting filters. Calibrated Newport 818-UV and Newport 818-IR power meters were used to measure the collimated output of a monochromator through a 1 mm aperture. The measurement bandwidth was \( \sim 40 \) nm and the intensity varied with the spectrum of the Xe lamp. The current vs. voltage response was
measured using the Keithley 2400 source-meters. The error in EQE measurements was estimated to be less than 5%.

Depth Profiling:

We used sputtering XPS for depth profiling of CQD devices prior to electrode deposition. The chemical composition of CQD films was characterized by Dr. Oleksandr Voznyy using a PHI VersaProbe II X-ray photoelectron spectrometer.

TGA experiments

Analysis was performed in collaboration with Dr. Jeffrey McDowell on a Perkin Elmer TL-2000 hyphenated TGA-GC-MS thermal analysis system. Helium is used as the carrier gas at flow rate of 1mL/min. Samples were thermalized using a Perkin Elmer Pyris 1 TGA system. The TGA was run using ~10-20 mg of sample in Pt pans. The TGA oven was purged with Helium at a rate of 100 mL/min during the run. TGA samples were held isothermally for 4 minutes at 50°C and ramped at 10°C /min until 900°C.

7.3 Simulations

Detailed Balance Analysis:

We used a MATLAB to establish our model and calculate thermodynamic limits and optimal bandgaps. An ideal absorber with a step function
absorption spectra was assumed. In all calculations, the incident power of blackbody radiation was constant at 50 mW/cm$^2$ and photon emission profile was normalized to yield this radiation power.

Self-consistent 1D Optoelectronic Modeling:

We employed SCAPS for gradient-doped junction simulations and transport analysis of different device architectures.\textsuperscript{62,63} Device parameters used in our SCAPS simulations are included in Table 7.1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>MPA-PbS p-type</th>
<th>MPA-PbS n-type</th>
<th>TBAI-PbS p-type</th>
<th>TMAOH-PbS p-type</th>
<th>N-TiO$_2$</th>
<th>N-ZnO</th>
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<tr>
<td>Bandgap (eV)</td>
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<td>0.74</td>
<td>0.74</td>
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<tr>
<td>Electron Affinity (eV)</td>
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<td>4.9</td>
<td>4.3</td>
<td>4.4</td>
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<tr>
<td>Lifetime (μs)</td>
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<td>1</td>
<td>10</td>
<td>10</td>
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</tr>
<tr>
<td>Electron Mobility (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>5x10$^{-3}$</td>
<td>5x10$^{-3}$</td>
<td>10$^{-4}$</td>
<td>1</td>
<td>1</td>
<td></td>
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<tr>
<td>Hole Mobility (cm$^3$V$^{-1}$s$^{-1}$)</td>
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<td>10$^{-4}$</td>
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<tr>
<td>Thickness(nm)</td>
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<td>300</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

Capacitance vs. voltage measurement did not provide a well-defined linear region to determine a precise value for doping. Thus, we proceeded with our modeling based on an approximate value of $\sim$10$^{15}$ - 10$^{16}$ cm$^{-3}$ n-doping for TBAI-PbS and $\sim$10$^{17}$ for MPA-PbS films.
8 References


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