To Xiaochang Miao
ACKNOWLEDGMENTS

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<tr>
<td>Ac</td>
<td>Acetate</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AM</td>
<td>Air mass</td>
</tr>
<tr>
<td>AR</td>
<td>Aspect ratio</td>
</tr>
<tr>
<td>BDT</td>
<td>Benzenedithiol</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>BR</td>
<td>Bimolecular recombination</td>
</tr>
<tr>
<td>BOS</td>
<td>Balance of system</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band, chlorobenzene (chapter 3)</td>
</tr>
<tr>
<td>CELIV</td>
<td>Carrier extraction by linearly increasing voltage</td>
</tr>
<tr>
<td>CF</td>
<td>Chloroform</td>
</tr>
<tr>
<td>CIGS</td>
<td>Copper-indium-gallium-diselenide</td>
</tr>
<tr>
<td>CIS</td>
<td>Copper-indium-selenide</td>
</tr>
<tr>
<td>CPVs</td>
<td>Concentrated photovoltaics</td>
</tr>
<tr>
<td>CRZ</td>
<td>Charge recombination zone</td>
</tr>
<tr>
<td>CS</td>
<td>Charge separation</td>
</tr>
<tr>
<td>CT</td>
<td>Charge transfer</td>
</tr>
<tr>
<td>C-V</td>
<td>Capacitance – voltage</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DA</td>
<td>Donor-acceptor</td>
</tr>
<tr>
<td>DAP-E</td>
<td>Secondary phosphine chalcogenides, Dialkylphosphine chalcogenides</td>
</tr>
<tr>
<td>o-DCB</td>
<td>o-dichlorobenzene</td>
</tr>
<tr>
<td>DIO</td>
<td>1,8-Diiodooctane</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-sensitized solar cells</td>
</tr>
<tr>
<td>EDT</td>
<td>Ethanedithiol</td>
</tr>
<tr>
<td>EFG</td>
<td>Edge-defined film-fed growth</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>ETA</td>
<td>Extremely thin semiconductor absorber</td>
</tr>
<tr>
<td>FETs</td>
<td>Field-effect transistors</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>GR</td>
<td>Germinate recombination</td>
</tr>
<tr>
<td>HTMs</td>
<td>Hole-transporting materials</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ICBA</td>
<td>Indene-C60 bisadduct</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LCOE</td>
<td>Levelised cost of electricity</td>
</tr>
<tr>
<td>LED</td>
<td>Light-emitting diodes</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MEG</td>
<td>Multi-exciton generation</td>
</tr>
<tr>
<td>MCCs</td>
<td>Molecular chalcogenide complexes</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Poly(2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene)</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular orbital</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NC</td>
<td>Nanocrystals</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infrared</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>J-V</td>
<td>Current density - voltage</td>
</tr>
<tr>
<td>OA</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>ODE</td>
<td>1-Octadecene</td>
</tr>
<tr>
<td>ODT</td>
<td>1, 8-Octanedithiol</td>
</tr>
<tr>
<td>OPVs</td>
<td>Organic photovoltaic cells</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexyl thiophene)</td>
</tr>
<tr>
<td>PA</td>
<td>Phosphonic acid</td>
</tr>
<tr>
<td>PC61BM</td>
<td>C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCE, or $\eta_p$</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>Poly((9-(1-octynonyl)-9H-carbazole-2,7-diyl)-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl)</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>Poly(2,1,3-benzothiadiazole-4,7-diyl(4,4-bis(2-ethylhexyl)-4H-cyclopenta(2,1-b:3,4-b') dithiophene-2,6-diyl))</td>
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<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)</td>
</tr>
<tr>
<td>PSCs</td>
<td>Polymer solar cells</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>PPA</td>
<td>$P, P'$-(di-$n$-tetradecyl) dihydrogen pyrophosphonic acid</td>
</tr>
<tr>
<td>QDs</td>
<td>Quantum dots</td>
</tr>
<tr>
<td>SCLC</td>
<td>Space charge limited current</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SILAR</td>
<td>Successive ion layer adsorption and reaction</td>
</tr>
<tr>
<td>SM</td>
<td>Small molecule</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
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<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>SSSC</td>
<td>Solid-state sensitized solar cells</td>
</tr>
<tr>
<td>TBP</td>
<td>Tributylphosphine</td>
</tr>
<tr>
<td>TBP-E</td>
<td>Tributylphosphine chalcogenides</td>
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<td>TDPA</td>
<td>Tetradecylphosphonic acid</td>
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<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TMAH</td>
<td>Tetramethylammonium hydroxide</td>
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<tr>
<td>TMOs</td>
<td>Transition metal oxides</td>
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<tr>
<td>TMS-E</td>
<td>Bis( trimethylsilyl ) chalcogenides</td>
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<tr>
<td>TOF</td>
<td>Time-of-flight</td>
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<tr>
<td>TOP</td>
<td>Triocetylphosphine</td>
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<td>TOPO</td>
<td>Triocetylphosphine oxide</td>
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<td>TOPS</td>
<td>Triocetylphosphine sulfide</td>
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<td>TOPSe</td>
<td>Triocetylphosphine selenide</td>
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<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Short-circuit current density, mA/cm$^2$</td>
</tr>
<tr>
<td>$n$</td>
<td>Electron concentration</td>
</tr>
<tr>
<td>$\eta_A$</td>
<td>Absorption efficiency</td>
</tr>
<tr>
<td>$\eta_{CT}$</td>
<td>Charge transfer / exciton dissociation efficiency</td>
</tr>
<tr>
<td>$\eta_{ED}$</td>
<td>Exciton diffusion efficiency</td>
</tr>
<tr>
<td>$\eta_{EQE}$</td>
<td>External quantum efficiency</td>
</tr>
</tbody>
</table>
\( n_i \)  
Intrinsic carrier concentration

\( \eta_{IQE}, \text{IQE} \)  
Internal quantum efficiency

\( \eta_p, \text{PCE} \)  
Power conversion efficiency

\( P_0 \)  
Illumination intensity

\( p \)  
Hole concentration

\( \text{R}_{\text{rms}} \)  
Root-mean-square roughness

\( V_{oc} \)  
Open-circuit voltage, V

\( V_{CB} \)  
Volume of chlorobenzene
Organic-inorganic hybrid materials that can potentially combine the low-cost and processing versatility of organic materials with high electronic performance and stability of inorganic semiconductors have been extensively used as active layer in photovoltaic cells, light-emitting diodes, and photodetectors. This dissertation endeavors to better understand operation mechanism as well as improve the performance of organic-inorganic hybrid photovoltaic cells using blends of conjugated polymers/oligomers and colloidal inorganic nanocrystals.

First, we study the effect of colloidal-synthesized CdSe nanocrystals on the performance of hybrid photovoltaic cells. The device using poly(3-hexylthiophene) and CdSe shows nanocrystal-size dependent performance and a maximum power conversion efficiency ~2.0% that attributes to improved charge transport and organic-inorganic hybrid morphology as well. The study has been extended to improve device performance by including a solution-processed ZnO nanoparticle layer between the hybrid active layer and the cathode, as a result of combinational optical, electrical, and morphological effects. Further enhancement in device performance has been achieved by selecting conjugated polymers with low energy gap and energy levels better aligned
with CdSe nanocrystals. The device using a low-gap polymer shows spectral response up to \(~850\) nm and a power conversion efficiency 3.5\%; and the device using a polymer with deep highest occupied molecular orbitals leads to an open-circuit voltage as high as 0.9 V.

Organic-inorganic interface that governs exciton dissociation (charge transfer) and charge transport in hybrid photovoltaic cells has been particularly emphasized. First, we introduce chemical treatment to engineer the organic-inorganic interface, which leads to a 30-90\% enhancement in device performance and a record-high power conversion efficiency 5\% in bulk heterojunction hybrid photovoltaic cells. Moreover, we also designed conjugated oligomers with functional groups to directly interface colloidal nanocrystals for hybrid photovoltaic cells.

Finally, tungsten oxide thin film was prepared by depositing precursor solution into supporting substrates and then thermally annealed at a mild temperature. Organic photovoltaic cells using these tungsten oxide thin films as anode interlayer have shown performance comparable to those using traditional organic interlayer.
CHAPTER 1
INTRODUCTION OF PHOTOVOLTAIC TECHNOLOGY

1.1 Introduction

Searching for clean, reliable, renewable, and affordable energy has become a critical state strategy for most of the countries in the 21st century. Fossil fuels including coal, oil and natural gas are non-renewable, highly carbon-emitted, and region-limited. The proven reserves are not able to meet the demand of the rapid growing in global economy and population in the next one century. Nuclear energy, though it is clean, could lead to a series of safety and subsequent environmental problems. Wind energy, hydropower, and geothermal energy, are clean and renewable if utilized properly, but they are location-limited. Harvesting energy directly from the Sun is the only approach to meet the requirement of both sustainable growth in human society and maintenance of a clean and healthy environment. However, even renewable energy technology has shown significant progress in the past several decades, fossil energy has still dominated our energy consumption style nowadays, as which possesses >85% of all consumption energy (Figure 1-1).¹

Photovoltaics or solar electricity, one of the renewable energy produced directly from the Sun, have shown rapid growth since the first demonstration of modern PV cells in silicon in the 1950s.² The electricity generated by photovoltaics is compatible to a range of applications including on- and off-grid, is not constraint to climate and geographic location, and has relatively low maintenance and operation cost. A PV system contains PV cells (or modules) and auxiliary components called balance of system (BOS) including inverter, batteries, mechanical structure, etc. Nowadays, the first generation and second generation PV modules have already went into market, and
Figure 1-1. (color) Statistics of energy consumption in the world. Fossil energy (oil, coal, and natural gas) still contains more than 80% of the world’s main energy consumption, which is predicted to decrease to 75% in 2035 as the fraction of renewable energy grows. Other renewables include wind, solar cells, solar thermal, etc. Adapted from World Energy Outlook 2011, International Energy Agency.

According to the data from International Renewable Energy Agency, the thin-film PV module prices had fallen below $1/watt to $0.84 – 0.93 /W, and the prices of the crystalline-Si modules varied in the range of $1.02/W - $1.24/W at the beginning of 2012. Even excluding the huge price drop due to the market factor (excess supply than demand), these prices still have a gap to the cost of the Sunshot initiative created by US Department of Energy in 2010, which suggested the cost of solar modules could be reduced to $0.50/W and the levelised cost of electricity (LCOE) to $1/W by 2020. Thus, together with the diffuse nature of the sunlight, further improving this technology is still a must to optimize the energy consumption in our only earth.

1.2 Status of Photovoltaic Technologies

The modern PV technology started in crystalline Si based on pn junctions in the 1950s, and subsequently other materials such as GaAs, CdTe, Cu$_2$S/CdS etc. had also
been developed for PV application in a fast manner. The power conversion efficiencies of the PV cells based on these inorganic semiconductors had reached to or above 10% at the first twenty years (Figure 1-2), which together with the driving by the energy crisis and pursuit of renewable energy by many countries led to the emerging, progress, and mature of the PV industry in the 1980s. PV module production was firstly realized in Si pn junction, which has been well known as first generation PV technology. Though several other PV technologies have been developed for module production, crystalline Si modules (c-Si) still have the dominant share in PV market nowadays. The early attempt to scale up the thin film PV technologies from laboratory centimeter square to module is not successful; while nowadays thin film PV modules based on amorphous Si (α-Si), CdTe, copper-indium-selenide (CIS) and copper-indium-gallium-diselenide (CIGS) that are known as second generation PV technology have become the major competitor of the c-Si modules.

The primary effort in PV industry is to increase the efficiency of the module and simultaneously reduce the cost of materials and production. The efficiency of single junction solar cells is constraint to the Shokley-Queisser limit derived by considering the loss in spectral coverage, exciton/charge recombination and black-body radiation. For example, Si solar cells have the Shokley-Queisser limit of 32.7%. Black-body radiation accounts for 7% when the device operated at room temperature, and this temperature-dependent loss is unavoidable. Spectrum loss and recombination can be engineered in terms of materials and device architecture to break this limit and maximize the efficiency. For example, staking cell in series with each subcell absorbing a specific wavelength range of photons is a practical approach to maximize absorption and
ultimately enhance efficiency. In fact, though multi-junction GaAs-based cells have shown very high efficiency (>30%), the high manufacture cost makes it only accessible to the application in aerospace and military industry. In addition, reducing exciton and charge recombination requires more optimal morphology or crystal quality of semiconductors and the better contact between the semiconductor and metal electrode. The semiconductor materials, fabrication, operation mechanism, and characterization of the PV cells will be surveyed in the following parts to evaluate the advantage and disadvantage of the different types of PV technologies.

1.3 Photovoltaic Materials and Devices

1.3.1 c-Si Photovoltaic Cells

Silicon, an abundant element in the earth, plays the most important role in the modern technology revolution. Si has an indirect bandgap of 1.1 eV and can be manufactured in a very large quantity at low-cost and with ultra-high purity. The production of c-Si solar cells mainly includes the Si ingot/wafer production, PV cell
fabrication, and module assembly. In general, c-Si can be classified as single crystalline Si (sc-Si), multicrystalline Si (mc-Si), and edge-defined film-fed growth (EFG) ribbon Si. The highest cell efficiencies of sc-Si and mc-Si are 25% and 20% (Figure 1-2), respectively, however, the efficiency of their commercial modules is typically 14-19%.

Figure 1-3a shows the device structure of a crystalline-Si solar cell. Slim metal grid at the illumination side forms one contact to the diode and allows sunlight to touch the semiconductor for harvesting. An antireflective layer is typically coated to reduce the absorption loss due to reflection in Si surface. The semiconductor diode contains an n-type and a p-type semiconductor, which touches each other to form a metallurgical junction or pn junction that is the basic for an inorganic solar cell.

In principle, when the semiconductor active layer absorbs a solar photon with energy higher than its band gap, an electron in valence band (VB) will be excited to empty conduction band (CB), resulting in the generation of a weakly-bounded electron-
hole pair called exciton. The photogenerated exciton subsequently dissociates into free electron and hole in an ultrafast manner (~$10^{-12} - 10^{-15}$ s), which will diffuse or drift under electrical field to the opposite collecting electrodes. Charge recombination could occur during the transport process. The collection of these photogenerated charge carriers leads to the photocurrent in the device and also photovoltage built-up across the two electrodes.

The absorption coefficient as a reflection of the photogeneration in a semiconductor with desired thickness for direct transition can be described by

$$\alpha(h\nu) \approx A(h\nu - E_g)^{1/2}$$

(1-1)

where $A$ is a constant, $h$ is Plank constant, $\nu$ is frequency, $E_g$ is the band gap of a semiconductor. For an indirect semiconductor, the absorption also involves the photon absorption or emission with required momentum. Thus, the absorption coefficient can be described as

$$\alpha(h\nu) = \alpha(\nu) + \alpha_e(h\nu) = \frac{A(h\nu - E_g + E_{ph})}{e^{E_{ph}/kT} - 1} + \frac{A(h\nu - E_g - E_{ph})}{1 - e^{-E_{ph}/kT}}.$$

(1-2)

Thus, for Si solar cells, the indirect band gap requires very thick active layer (hundreds of micrometers) to harvest most of the sunlight.²

Recombination is an important electronic process occurred in solar cells and the very process leading to loss in photocurrent. The mechanism includes recombination through traps in the forbidden gap, radiative recombination, and Auger recombination. The net recombination rate through a single level trap within the forbidden gap can be expressed as

$$R = \frac{n^2 - n_i^2}{\tau_n(p + n_i e^{-E_i/kT}) + \tau_p(n + n_i e^{-E_i/kT})}.$$

(1-3)
where \( p, n, \) and \( n_i \) are the concentration of hole, electron, and intrinsic carriers, respectively; and carrier lifetime is given by \( \tau = \frac{1}{\sigma u_{th} N_T} \), where \( \sigma \) is the capture cross section, \( u_{th} \) is the thermal velocity of the carriers, and \( N_T \) is the concentration of the traps. Note that the recombination rate is only dependent on the minority carrier, the recombination rate for a p-type semiconductor in low-injection condition can be simplified as \( R \approx \frac{n-n_i}{\tau_n} \). The net recombination rate due to radiative processes is given by

\[
R = B(pn - n_i^2) \tag{1-4}
\]

where \( B \) is a constant, and for a p-type semiconductor at low-injection condition, the equation can be re-written as \( R \approx \frac{n-n_i}{\tau_n} \), where \( \tau_n = \frac{1}{p_0 B^2} \).

The net recombination rate due to Auger process is given by

\[
R = (\Lambda_n n + \Lambda_p p)(pn - n_i^2) \tag{1-5}
\]

Thus, the total recombination rate in a semiconductor is the sum of these individual rates.

The carrier transport in conventional inorganic semiconductors includes drift and diffusion processes. The drift velocity is proportional to the electric field and related to carrier mobility. The driving force for diffusion is the difference in carrier concentration and in thermal equilibrium, and the diffusion coefficient (D) can be expressed by Einstein relationship (Chapter 3). In solar cells, lattice and ionized impurity scattering are the main scattering mechanism in carrier transport.

By solving the minority-carrier diffusion equation together with appropriate boundary conditions, the current – voltage characteristics for an inorganic solar cell can be derived as
\[ I = I_{sc} - I_{o1} \left( e^{\frac{qV}{ekT}} - 1 \right) - I_{o2} \left( e^{\frac{qV}{ekT}} - 1 \right) \]  

(1-6)

where \( I_{o1} \) and \( I_{o2} \) are the saturated dark current due to recombination in the quasi-neutral region and in the space-charge region, respectively.\(^2\)

### 1.3.2 Thin Film Photovoltaic Cells

The high cost in both materials processing and device fabrication of c-Si cells stimulates to develop other PV technologies. Thin film solar cells then gradually move to the commercial stage for their advantages such as low material usage (<1% thick of c-Si cell), low manufacturing cost (potential wet-chemistry processing), and compatible with a variety of light-weight and even flexible supporting substrates. Nowadays three types of thin film solar cells including amorphous Si (α-Si), CdTe, and CIGS have been commercially developed with high efficiency (Figure 1-2). Here we exemplify the fabrication and principle of the CIGS cells.

Figure 1-3b shows the device structure of a typical CIGS cell. The back contact Mo layer that is very sensitive to water is deposited by sputtering at high vacuum. The CIGS layer is typically deposited by multi-source co-evaporation and two-stage processes of precursor deposition followed by selenium annealing. A thin CdS layer is deposited by chemical bath deposition to form the CIGS-CdS junction. Due to the environmental safety concern, CdS has also been replaced by Cd-free compounds such as ZnS, ZnO, ZnSe, etc. However, the deposition limit of these Cd-free compounds makes CdS still the priority choice, since it can protect the active layer and the junction during the subsequent depositions. A thin ZnO window layer with high resistance (1-100 \( \Omega \cdot \text{cm} \)) deposited by radio frequency magnetron sputtering is used to improve the diode quality. It is argued that if the CdS layer is thick enough, the ZnO layer is not necessary.
to improve device performance. Then a doped high-conductivity ZnO layer are
deposited by sputtering or chemical vapor deposition, followed by deposition of Ni/Al
grid to enhance charge collection.²

Though efficiency of laboratory cells has reached to 20% by optimization in
materials processing and device fabrication, the underlying operation mechanism is still
not fully understood. Photogeneration occurs at the CIGS layer and the space charge
region at the CIGS layer and also CdS layer leads to the charge separation. The
photogeneration loss is typically due to the surface and front metal grid reflection, the
absorption in the CdS layer and TCO layer, and the incomplete absorption in CIGS
layer. The recombination loss reflects in the open-circuit voltage, which is also a
function of the band gap of the CIGS.² Recombination typically occurs at the defects
and imperfect structure in the CIGS layer, while the recombination at the CIGS-CdS
junction is trivial by proper doping. In addition, the grain boundaries in the CIGS layer
could also affect the transport and recombination. The CdS layer creates the type
inversion at the CIGS-CdS interface and is fully depleted. The band alignment at the
CIGS-CdS indicates that the energy offset at the CB (ΔEc) is of importance in creating
the type inversion.

Other than using high vacuum and high temperature deposition method for the
CIGS layer, recently Mitzi and co-workers developed a precursor approach to deposit
CIGS layer through solution processing.⁵,⁶ These solution-processed cells maintain the
conventional CIGS structure and show efficiency 10-15%, which makes this technology
more promising for future photovoltaics. Due to the high cost in indium, the alternative
absorbers with earth-abundant element such as copper-zinc-tin-selenide (CZTSe) have also been developed with high efficiency. 6, 7

1.3.3 Third Generation Photovoltaic Cells

Third generation photovoltaic technologies are mostly at the laboratory research stage yet grow in a fast pace recently. The third generation PV technologies generally include concentrated photovoltaics (CPVs), dye-sensitized solar cells (DSSC), organic solar cells (OPVs), and other novel and emerging solar cell concepts such as quantum dot solar cells (Chapter 2.6), intermediate band cells, etc. 3 The CPVs utilize the optical devices to concentrate the sun light into a small but high-efficiency multi-junction cell.

The optical devices need to be oriented to the sun and cooling system is necessary to reduce the performance loss due to high operation temperature. Since it focuses on the optical management, rather than introducing new materials or new concept in PV technologies, we do not intend to discuss in detail about CPVs. Instead, we will particularly introduce DSSC and OPVs as examples of the development of third generation PV technologies.

1.3.3.1 Dye-sensitized solar cells

Dye-sensitized solar cells (DSSC) have received significant attention as major advancement made by Grätzel and co-workers in the early 1990s. 8, 9 In a typical manner, it consists of a transparent conductive substrate such as fluorine-doped SnO₂, a photoelectrode such as mesoporous TiOₓ thin film, a photosensitizer such as Ru complex, a redox electrolyte such as I⁻/I₃⁻ redox ions, and a counter electrode with high electrocatalytic activity such as Pt (Figure 1-4).

When illuminated, Ru complex photosensitizer absorbs the incident photons and is excited from a ground state to an excited state, following by the injection of the
Figure 1-4. (color) Schematic illustration of device structures of dye-sensitized solar cell using either liquid (left) or solid electrolyte (right). The solid-state DSSC may have a thin absorber layer and a hole transporting layer, here we simplify them as solid electrolyte layer.

excited electron to TiO$_x$ CB. These electrons then transport to the TCO through diffusion in TiO$_x$ and ultimately reach to the counter electrode through the external loading. The oxidized photosensitizer then accepts electron from an I$^-$ ion redox mediator to regenerate the ground state, and simultaneously the I$^-$ is oxidized to I$_3^-$. The oxidized redox mediator is re-reduced to I$^-$ ion by diffusing to the counter electrode. Overall, the incident photon is converted to electron with retained chemical states of the involving materials.

The energy gap of the photosensitizer determines the photocurrent, and the energy offset between the Fermi level of TiO$_x$ and redox potential of the mediator determines the output voltage. The energy offsets between the photosensitizer LUMO and TiO$_x$ CB and between the redox mediator potential and the photosensitizer HOMO should be sufficient high (> 200 mV) for efficient charge injection / electron-transfer reaction. Unlike conventional inorganic solar cells and organic solar cells as well, only electron is generated in photosensitizer and directly injected to TiO$_x$, which leads to the
absence of charge recombination process and of electric field for charge separation.\textsuperscript{9} Besides, charge transport occurs in TiO\textsubscript{x} phase that is different to the photogeneration sites, which leads to the very efficient charge separation.

Though the efficiency of liquid DSSC has reached to > 10\% even in a submodule level,\textsuperscript{4} the durability and safety of this type of cells is a big concern since the liquid electrolyte may cause potential corrosion and leakage. DSSC utilizing solid-state electrolytes (SSSC) then have received much attention (Figure 1-4).\textsuperscript{10} Organic, inorganic, and organic-inorganic hybrid semiconducting and hole-transporting materials (HTMs) have been developed as solid-state electrolyte and even as light absorber. Instead of using organic dye or solid state HTMs as light absorber, an extremely thin semiconductor absorber (ETA, < 50 nm) is typically coated upon the TiO\textsubscript{x}. The mechanism in SSSC is not fully proven yet it may share some elements of DSSC. Recently SSSCs with efficiency 10\% using newly-developed p-type direct bandgap semiconductor CsSnI\textsubscript{3} as HTMs and the dye N719 as absorber or spiro-OMeTAD as p-type hole conductor and organic-inorganic hybrid perovskite (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{2}Cl) as ETA have been reported,\textsuperscript{11,12} suggesting the promising commercialization of this type of cells in the near future.

1.3.3.2 Organic solar cells

Organic photovoltaic cells that utilize organic small molecule or polymer to harvest solar photons have received considerate attention since the first bilayer structured cell with efficiency >1\% invented by Tang in the 1980s.\textsuperscript{13} The laboratory efficiency has reached to ~10\% for organic PV cells based on either vacuum-deposited small molecules or solution-processed polymers (Figure 1-2).\textsuperscript{4} The difference in operation principle compared to inorganic solar cells mainly lies in the difference in
fundamental physical properties between organic and inorganic semiconductors. OPVs require a donor-acceptor heterojunction for charge transfer and separation and the separated charges transport individually at the donor and acceptor components to the respective collecting electrodes.\textsuperscript{13, 14} The operation principles and research progress will be detailed in Chapter 3.

Compared to PV technologies based on inorganic semiconductors, the advantages of the OPVs are self-evident: organic materials are cheap, abundant, tailorable, processable, flexible, and light-weight; OPVs can be manufactured using roll-to-roll processing in a variety of substrates including flexible substrates (Figure 1-5), be semi-transparent, and be ultrathin (100 – 200 nm in organic active layer).\textsuperscript{15} The flexible and light-weight nature enables to install the OPVs in various places including roof, window, bus station, bag, or even the back of electronic devices, etc. However, the challenge of OPV is also very straightforward: the relatively low efficiency, particularly in module and the stability of both organic materials and devices.
1.4 Organic-inorganic Hybrid Photovoltaic Cells

The relatively low mobility and dielectric constant in organic semiconductors are the main reasons for the loss in photocurrent and photovoltage in organic photovoltaic cells. On the contrary, inorganic semiconductors have high electronic performance due to their high mobility and dielectric constant and high environmental stability as well. Thus, combining the advantages of high electronic performance and stability of inorganic semiconductors with processing flexibility and high absorption coefficient of organic semiconductors is the right pursuit for the new generation of mesoscale materials in optoelectronic application. Organic-inorganic hybrid photovoltaic cells, thanking to the advent of the solution-processable colloidal nanocrystals, have then emerged as an alternative to all organic solar cells in the beginning of this century.\(^\text{16}\)

The first polymer-nanocrystal hybrid solar cell with bulk heterojunction structure was demonstrated by Greenham et al. in 1996 with efficiency $< 0.1\%$.\(^\text{17}\) In 2002 Alivisatos and co-workers demonstrated polymer-nanorod PV cells with $\eta_p 1.7\%$ under AM 1.5G 1 sun illumination.\(^\text{16}\) This conceptual publication together with rapid progress in nanocrystal synthesis has then fueled much research interest in photovoltaic application of polymer:nanocrystal hybrid materials. Though the progress is in a slow and zigzag pace, the $\eta_p$ has reached to a level of 3-5% in this community by tailoring colloidal nanocrystals and conjugated polymers, engineering polymer-nanocrystals interface, and optimizing device architecture.\(^\text{18}\)

The operation mechanism is similar to polymer solar cells and based on the organic-inorganic (polymer-nanocrystal) donor-acceptor junction. Conjugated polymers serve as electron donors and hole-transporting materials, and colloidal nanocrystals serve as electron acceptors and transporter. Photogeneration occurs both in conjugated
polymers and colloidal nanocrystals once the incident photons have energy higher than their energy gaps; and charge transfer happens at a polymer-nanocrystal interface. The separated electron and hole then transport in nanocrystal phase and polymer phase, respectively, and then are collected by the corresponding electrodes. Nonetheless, compared to all organic solar cells, the involvement of nanocrystals creates an organic-inorganic interface that has been recognized as main challenge in the advancement of this technology. This organic-inorganic interface includes the chemical, morphological, and electronic interfaces, and thus far all of these are still not well understood, which will be particularly surveyed in this dissertation.

1.5 Characterization of Photovoltaic Cells

1.5.1 Current - Voltage Measurement and Photovoltaic Parameters

Current – voltage (I-V) measurement is typically used to determine the diode characteristics and critical performance parameters of a PV cell. The test cell in the dark or under illumination is biased with variable voltage load and the current is sensed by an Agilent semiconductor parameter analyzer. The simulated AM 1.5 G solar illumination is provided by using a Xe-arc lamp. The intensity of solar illumination is calibrated using a standard Si PV test cell equipped with a series of neutral density filters. A KG1 filter has been used to match the solar spectrum. The spectral mismatch between the simulated and standard solar spectrum for particular materials system has been corrected, as discussed in the following part.

As the equivalent circuit shown in Figure 1-6a, a PV cell can be modeled as an ideal diode with a parallel current source due to photocurrent (Jph), a parallel shunt resistance (Rsh) due to the leakage current, and a series resistance (Rs) due to finite conductivity of semiconductors and the contact resistance between semiconductors and
electrodes. The series resistance and shunt resistance of the PV cells can be obtained by fitting the $J - V$ curves as shown in Figure 1-6b through the Schottky equation:

$$J = J_s \left\{ \exp \left[ \frac{q(V - jR_s)}{nkT} \right] - 1 \right\} + \frac{V - jR_s}{R_{sh}} + J_{ph}$$

(1-7)

where $J_s$ is the saturation current density of the ideal diode, $n$ is the ideality factor, $k$ is Boltzmann’s constant, and $T$ is the absolute temperature.

The PV performance parameters including short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$) and fill factor (FF) can be extracted directly from the $J - V$ characteristic under illumination. Power conversion efficiency ($\eta_p$) that is the ratio of the maximum electrical power output ($P_{m,out}$) to the incident optical power density ($P_0$) can be calculated by the expression

$$\eta_p = \frac{P_{m,out}}{P_0} \times 100\% = \frac{J_{sc} \times V_{oc} \times FF}{P_0} \times 100\%$$

(1-8)

where $J_{sc}$ is the short-circuit current density and $V_{oc}$ is the open-circuit voltage, both of which can be directly obtained from $J - V$ characteristics; FF is the fill factor, which is the squareness of the $J - V$ characteristics.

Figure 1-6. Equivalent circuit (a) and typical $J - V$ curves (b) of a PV cell. Here $R_s$ is the series resistance, $R_{sh}$ is the shunt resistance, $J_{ph}$ is the photocurrent.
For an ideal PV cell with \( R_s = 0 \) and \( R_{sh} = \infty \), the photocurrent is directly proportional to the incident power intensity, namely, \( J_{sc}/P_0 = \) constant; and the \( V_{oc} \) can be derived with the following expression:

\[
V_{oc} = \frac{n k T}{q} \ln \left( \frac{J_{ph}}{J_s} + 1 \right) \propto \ln P_0. \tag{1-9}
\]

### 1.5.2 Solar Spectrum

The emission of radiation from the sun is similar to the black-body radiation, and the light reaching the Earth surface can be approximated as parallel streams of solar photons due to the far distance between the Sun and the Earth. Since the atmosphere absorption can affect the spectral content and intensity of the solar radiation reaching the Earth surface, air mass (AM) has been introduced to define the actual spectral content and intensity. The AM 1.5 G spectrum normalized to a power density of 100 mW/cm\(^2\) (1 sun) has been widely used as a standard for comparing solar cell performance (Figure 1-7). Here G (global) means the measured spectrum includes the diffuse component yet D (direct) does not.

In fact, the spectrum of the simulated AM 1.5G solar illumination from Xe-arc lamp even after filtering is not well matched with the reference spectrum (Figure 1-7). The absorption coefficient and range of organic semiconductors are also vastly different from Si materials. Hence, in order to accurately determine the illumination intensity, a spectral mismatch factor has been introduced and expressed as

\[
M = \frac{\int_{\lambda_1}^{\lambda_2} E_R(\lambda) S_R(\lambda) \, d\lambda \cdot \int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_T(\lambda) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} E_R(\lambda) S_T(\lambda) \, d\lambda \cdot \int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_R(\lambda) \, d\lambda} = \frac{I_{R,R} \cdot I_{S,T}}{I_{R,T} \cdot I_{S,R}} \tag{1-10}
\]

where \( E_R \) is the reference spectral intensity, \( E_S \) is the simulated source intensity, \( S_R \) is the spectral responsivity of Si cell, \( S_T \) is the spectral responsivity of test PV cell that is
calculated from EQE by \( S_T(\lambda) = \frac{q \lambda}{h c} \eta_{EQE}(\lambda) = 8.0655 \times 10^5 \cdot \lambda \cdot \eta_{EQE}(\lambda) (A/W) \). Each function must be integrated over the photoresponse wavelength of the test cell. By adjusting the solar simulator spectral irradiance, \( I^{R,R} \) can be equal to \( I^{S,R} \). Hence, the real \( I_{sc}(I^{R,T}) \) of the test cell under the reference cell can be expressed as

\[
I^{R,T} = \frac{I^{R,R}}{I^{S,R}} \times \frac{I^{S,T}}{M} (I^{R,R} = I^{S,R}) \tag{1-11}
\]

Though there is some difference in reference and simulated spectra, the \( M \) in organic-based solar cell is close to unity for most of the material systems. The \( M \) of some material systems for organic-based solar cells in this study has been listed in Table 1-1.

### 1.5.3 Quantum Efficiency

Quantum efficiency measurement is another characterization technique to

<table>
<thead>
<tr>
<th>Active layer</th>
<th>P3HT:PCBM</th>
<th>P3HT:CdSe</th>
<th>PCPDTBT:CdSe</th>
<th>CuPc/C60</th>
<th>SubPc/C60</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M )</td>
<td>0.98</td>
<td>0.99</td>
<td>0.98</td>
<td>0.99</td>
<td>0.98</td>
</tr>
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assess performance of a PV cell. The photoresponse range and intensity of the cell can be revealed through QE study. The light illuminated from halogen lamp passes through monochromator to give a low intensity light (1-10 μW/cm²) with desired wavelength. The monochromatic light has been mechanically chopped at 400 Hz before shining upon a calibrated Newport 818-UV Si detector for overall intensity measurement (I₀) or a test device for photocurrent measurement (I₉). A Stanford Research Systems 830DSP lock-in amplifier with synchronous frequency of the mechanical chopper, together with a Keithley 428 current amplifier to reduce noise/signal ratio, has been used to monitor the photocurrent of the device. The test devices were also illuminated by a separate constant white light bias from a halogen lamp with an intensity of ~ 0.5 – 1 sun to create similar optical and electric fields as I – V measurement. Hence, the EQE can be calculated by

\[ \eta_{E QE} = \frac{\frac{h c}{q \lambda} \cdot \frac{I_d(\lambda)}{I_0(\lambda) / R_D(\lambda)}} \]

where \( h \) is Plank constant, \( q \) is the elementary charge, \( I_d(\lambda) \) is the photocurrent of the test device at a given wavelength, \( I_0(\lambda) \) is the intensity of the Si detector at a given wavelength, \( R_D(\lambda) \) is the responsivity of the Si detector at a given wavelength. The short-circuit current density of the test cell under reference 1 sun (= 100mW/cm²) AM 1.5G illumination can also be calculated using EQE through the expression

\[ I_s = \int_{\lambda_1}^{\lambda_2} \frac{q}{h c} \cdot \eta_{E QE}(\lambda) \cdot \lambda \cdot S(\lambda) d\lambda \]

(1-13)
where $S(\lambda)$ is the reference AM 1.5G power intensity. The difference between the $J_{sc}$ obtained from $J-V$ measurement and the $J_{sc}$ calculated from EQE should be very small if the simulator was calibrated correctly, typically within 5% in error (Figure 1-8).

The Si detector was used to measure the intensity of light before and after passing the test device. The absorbance of the device was calculated by

$$\eta_A = \frac{I_0(\lambda)-I_r(\lambda)}{I_0(\lambda)} \times 100\%$$

(1-14)

where $I_r(\lambda)$ is the reflective light measured by the detector.

![Figure 1-8. (color) The typical external quantum efficiency ($\eta_{EQE}$) of a bilayer CuPc/C60 solar cell. The integrated $J_{sc}$ from EQE is 4.0 mA/cm$^2$, which is almost the same as the $J_{sc}$ (3.9 mA/cm$^2$) determined from $J-V$ characteristics under 1 sun AM 1.5G illumination.](image)

1.6 Overview of This Dissertation

This dissertation focuses on photovoltaic cells using blends of organic semiconductors and colloidal nanocrystals. We intend to provide a better understanding on fundamental physical properties of organic-inorganic hybrid thin films and to demonstrate their unique feasibility in photovoltaic application. The first three chapters
provide the fundamental context for the coming work present in this dissertation. Chapter 4 to Chapter 9 can be generally divided into three parts: Chapter 4 to Chapter 6 focuses on the fundamental properties of organic-inorganic hybrid materials and their influence on the performance of hybrid PV cells; Chapter 7 and Chapter 8 strengthen on organic-inorganic interface engineering to enhance the hybrid PV cell performance; Chapter 9 studies the preparation of metal oxides as anode interfacial layer for organic-based PV cells.

In part I, first, Chapter 4 demonstrates the synthesis, processing, and properties of colloidal CdSe nanocrystals and their effect on the performance of organic-inorganic hybrid PV cells. Chapter 5 intends to enhance the performance of hybrid PV cells by including a solution-processed ZnO nanoparticle layer between the active layer and the cathode. Chapter 5 endeavors to enhance the photocurrent and photovoltage of hybrid PV cells in the perspective of conjugated polymers selection and processing.

The part II intends to address the fundamental issue of organic-inorganic interface in hybrid PV cells. Chapter 7 focuses on engineering the polymer-nanocrystal interface by chemical treatment to enhance the performance of hybrid PV cells and to understand the fundamental chemical and physical mechanisms of the organic-inorganic interface. Chapter 8 further attempts to engineer the organic-inorganic interface by directly grafting conjugated oligomers with functional group to colloidal nanocrystals.

The part III including Chapter 9 introduces the low-temperature solution-processing of metal oxides as anode interfacial layer for organic-based PV cells. Organic-based PV cells using these solution-processed metal oxides have been
demonstrated with comparable performance to those cells based on traditional organic interlayer. Finally, Chapter 10 concludes this work and provides the future research directions for organic-inorganic hybrid photovoltaic cells.
CHAPTER 2
INTRODUCTION TO COLLOIDAL NANOCRYSTALS

2.1 Introduction

Crystalline semiconductor solids are the fundamental building blocks for modern electronics and optics. Further advances in the semiconductor industry will require the downsizing of these solids to a nanometer-scale regime. The fundamental properties of these solids become size-dependent when one of their dimensions reaches this scale.\textsuperscript{20-24} For example, the band gap of CdSe, a prototypical semiconducting solid, can be varied from 1.7 eV to 3.0 eV by simply tailoring its physical size yet maintaining the chemical composition.\textsuperscript{25,26} The size-dependent properties are the main stimulus for the wide-spread study, both in academia and in industry, of these nanoscale solids (nanocrystals) in the past two decades.\textsuperscript{21,23,27}

Colloidal nanocrystals are referred to solution-grown, organic-monolayer-stabilized, electronically-isolated, and nanometer-scale inorganic particles.\textsuperscript{18,27} These nanocrystals are composed of tens to thousands of atoms and bridge the gap between molecules and bulk crystals in both physical dimension as well as physical/chemical properties. Compared to their bulk counterparts, nanocrystals exhibit two main characteristics: i). the intrinsic properties of nanocrystals are subjected to the quantum confinement effect; ii). the surface properties of nanocrystals become more and more significant as the fraction of surface atoms increased with size decreasing and with the involvement of the stabilizing organic monolayer.\textsuperscript{21,26} Thus, this opens a great opportunity to tune the physical properties of the colloidal nanocrystals by simply adjusting their composition, size, shape, and surface ligands;\textsuperscript{26-31} the size-dependent properties combined with solution-processability also make nanocrystals a promising
candidate as building blocks for a variety of optoelectronic devices and as fluorophores in biomedical applications.\textsuperscript{32-35} In particular, this dissertation will focus on the synthesis and processing of colloidal nanocrystals for photovoltaic application.

In this chapter, though it is not intended to cover all the basic knowledge and technological breakthroughs, aims to provide a context for the work that will be presented concerning colloidal nanocrystals. The electronic structure and the synthesis of colloidal nanocrystals will be first introduced, followed by surveying the surface chemistry due to its critical importance of governing the physical properties and in a variety of application. The optical and electronic properties and the application in optical energy conversion devices will be also discussed.

2.2 Electronic Structure of Nanocrystals

Molecules are formed by chemically bonding atoms together. When two atoms approach each other to form covalent bond, according to molecular orbitals theory, the atomic orbitals interact to form bonding molecular orbitals (MO) and anti-bonding MO. The bonding electrons will preferentially reside on the lower-energy-level bonding MO and leave higher-energy-level anti-bonding MO empty (Figure 2-1), which minimizes the free energy of the new molecule. If these molecules assemble to form an infinite solid, the significant interaction of the MOs leads to the splitting of the energy levels; accordingly, the bonding and anti-bonding MOs of the molecule lead to the formation of two continuous energy levels valence band (VB) and conduction band (CB) of the solid. An energy gap or band gap ($E_g$) has simultaneously developed to separate the VB and CB. The VB will be occupied by the covalent electrons, and the CB will be unoccupied (Figure 2-1). For a bulk semiconductor, for example, Si, the absorption of a visible photon (energy higher than $E_g$) will excite a valence electron to the conduction band,
resulting in the formation of an electron-hole pair or exciton. Due to the high dielectric coefficient (ε), excitons formed in bulk inorganic semiconductors can be easily dissociated into two free polarons. Once generated, these free polarons together with their precursor excitons are highly delocalized among the crystalline solids.

However, the previous continuous energy levels of bulk solids, according to quantum mechanics, will be discretized for nanocrystals (Figure 2-1), and the density of electronic states (DOS) and energy gap correspondingly varied as the size varies. If the nanocrystal size is comparable to or less than its exciton Bohr radius (r_B) that is related to the effective electron and hole masses and dielectric coefficient, the photogenerated excitons will be spatially confined, rather than delocalized. This quantum confinement will more likely lead to exciton recombination for nanocrystals as a relaxation manner for the excited electrons, rather than exciton dissociation in bulk semiconductors. This argument has been well demonstrated in the state-of-the-art quantum dots (QDs), which show emission (radiative recombination process with an emissive photon) yield approaching unity. Also, the phenomenon that the emission

Figure 2-1. (color) The comparison of electronic energy states of a semiconductor at different length scales.
wavelength increases as the QDs’ sizes decrease indicates that the quantum confinement becomes more and more significant and energy level of the nanocrystals is more discretized.

According to the particle-in-a-box model, the band gap shift of nanocrystals can be approximately predicted by

\[
\Delta E \approx \frac{\hbar^2}{8\pi^2 R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon_R R}
\]

(2-1)

where \( \hbar \) is Planck’s constant, \( R \) the nanocrystal radius, \( e \) the elementary charge, \( \varepsilon \) the dielectric coefficient, and \( m_e^* \) and \( m_h^* \) the effective electron and hole masses, respectively.\(^{38} \) Thus, the band gap of nanocrystals can be calculated by

\[
E_{g,\text{nanocrystal}} = E_{g,\text{bulk}} + \Delta E \approx E_{g,\text{bulk}} + \frac{\hbar^2}{8\pi^2 R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon_R R}
\]

(2-2)

Since the Coulomb interaction term (decrease as \( R^{-1} \)) is relatively small compared to the quantum localization term (increase as \( R^{-2} \)), thus the band gap of the nanocrystals always increases as the size decreases.

2.3 Colloidal Nanocrystals Growth

2.3.1 Synthesis of Quantum Dots

Quantum dots refer to inorganic nanocrystals that confine excitons in all three spatial dimensions and exhibit size-dependent absorption and emission properties.\(^{21,31,38} \) Quantum dots have been studied since the pioneering of nanotechnology and are the typical starting morphology for investigating the properties of new nanoscale materials. A number of inorganic bulk materials can be tailored with nanometer dimensions that lead to new chemical and physical properties. For example, as shown in Figure 2-2, the
energy level and band gap of bulk materials can be engineered to follow the scaling rule.\textsuperscript{39, 40}

The formation of colloidal nanocrystals (including quantum dots) is generally governed by nucleation and growth in a system containing precursors, organic surfactants, solvents, and organic impurities originating from the source chemicals.\textsuperscript{27, 31, 41} The precursors are chemically transformed to active species upon heating to a desired temperature, which leads to nucleation after sufficient accumulation of these active species. Further growth is controlled by both the abundance of the active species and the organic surfactants. Most of the precursors are metal-organic complexes that can be decomposed at 50 – 350 °C \textsuperscript{42, 43} and the surface energy of solids in nanoscale could be significantly lower than in the bulk, it is feasible to colloidally generate nanocrystals at relatively low temperature at which the organic surfactants and solvents are stable.\textsuperscript{27, 44}

Thermal decomposition was the first strategy for colloidal synthesis of nanocrystals.\textsuperscript{27, 31, 41, 42, 45} To synthesize CdE (E = S, Se, and Te) nanocrystals, cadmium alkyls (dimethylcadmium) and bis(trimethylsilyl)chalcogenides were used as

![Energy levels of some common inorganic semiconductors](image)

**Figure 2-2.** (color) Energy levels of some common inorganic semiconductors. Due to the low band gaps of Pb-chalcogenides, their energy levels shown here correspond to the quantum dots with size 2-3 nm, which is also the dimension of interest for optoelectronic application.
Cd and chalcogen sources, respectively; and alkylphosphine oxides (triocetylphosphine oxide, technical TOPO) were selected as both solvent and surface capping ligand. In a similar manner, other metal alkyls such as diethylzinc and dibenzylmercury have been correspondingly chosen to produce other II-VI nanocrystals. It is worthwhile to mention that these metal alkyls are not decomposed into reactive specie directly, but rather, reacted with a trace of alkylphosphonic acid (PA, from technical TOPO) to form metal-PA complex as metal source precursors. Inspired by this observation, Peng et al. employed CdO together with phosphonic acids as starting chemicals to replace those toxic pyrophoric, hygroscopic, expensive, and unstable metal alkyls for producing high-quality CdE nanocrystals. Since then, other metal oxides and metal acetates (Ac) such as PbO, MnO, ZnO, CdCl$_2$, MnCl$_2$, PbCl$_2$, ZnCl$_2$, and Zn(Ac)$_2$ have also been gradually developed for nanocrystal synthesis.

Bis(trimethylsilyl) chalcogenides (TMS-E) and trialkylphosphine chalcogeneides such as trioctylphosphine selenide (TOPSe) and tributylphosphine selenide (TBPSe) are the typical choices as anion precursors. The recent work by Evans et al. revealed that the secondary phosphine chalcogenides (DAP-E, dialkylphosphine chalcogeneides), rather than tertiary phosphine chalcogenides (TBP-E and TOP-E) are the reactive species for the nuclei formation. The secondary phosphines exist as an impurity of the commercial TBP and TOP, which have been identified as vehicles for delivering chalcogenides (such as selenium) to the secondary phosphines during the reaction. This observation also paves a way to increase the nanocrystal yield by intentionally adding a required amount of secondary phosphine into tertiary phosphine for preparing anionic precursors. In addition, since the reactivity of the anionic precursors such as
TMS-E, DAP-E TOP-E, and TBP-E varies due to the difference in the P=E bond strength, synthesis of ternary or quaternary nanocrystals with uniform chemical composition and distribution can be realized by balancing this anionic precursors’ reactivity.48

Apart from the cationic and anionic components, organic ligands are another essential chemical component of colloidal nanocrystals. These organic ligands initially serve to stabilize the nanocrystals and may form a covalent, ionic, or dative bonding with the inorganic component. Carboxylic acids, alkylphosphosphate, alkylphosphine oxide, alkylthiols, and alkylamines are typical surface capping ligands.27, 31 During crystal growth, these ligands play mainly two roles: before nucleation, as mentioned, reacting with metal precursors to form reactive and decomposable precursors; after nucleation, ‘interfering’ with crystal growth through adsorption and desorption from nanocrystal surface. For example, the alkylphosphonic acid (PA), a highly-populated ligand on CdSe nanorods, first reacts with CdO to form Cd-PA complex as a cationic precursor; and then during nanocrystal growth specifically binds to some crystal planes that suppress their further growth and direct the nanocrystal growth on other exposed planes.28 It should be mentioned that during the nanocrystal growth there is a dynamic equilibrium between ligand-adsorption and ligand-desorption that is highly dependent on many factors such as nanoparticle-ligand binding strength, ligand-solvent interaction, steric hindrance, temperature, etc.29

The termination of nanocrystal growth has been realized by rapidly cooling the reaction mixture below a temperature threshold or diluting the monomer concentration. However, in many cases, Ostwald ripening could occur once the monomer becomes
depleted or its concentration decreases to a threshold, leading to the dissolution of the smaller nanocrystals and the further growth of larger nanocrystals. The control of monomer concentration, reaction temperature, and reaction time are rather empirical at this moment, and vary from one system to another. In spite of that, the size of nanocrystal can still be facilely controlled for almost all developed nanocrystals under the concept of size-distribution focusing growth. High monomer concentration will lead to the growth of smaller particles with a faster rate than that of larger ones, and consequently result in focusing of nanoparticles into monodispersity.

Though the coordinating solvents such as TOPO have exhibited great successes in the synthesis of CdSe nanocrystals, many studies have found that it is difficult to be extended to other nanocrystal systems with high quality. Non-coordinating solvents such as 1-octadecene (ODE) then have been utilized to address this issue. This synthesis strategy can be realized by utilizing elemental anionic precursors. The key advantage between coordinating and non-coordinating approaches is that the monomer reactivity can be tuned by controlling the ligand concentration in the non-coordinating solvent. Thus, the nucleation and growth can be better controlled for high-quality nanocrystal syntheses such as CdS, PbS, PbSe, etc.

Figure 2-3. Colloidally-synthesized CdSe nanostructures. Adapted with permission from Ref.26. Copyright 2010 American Chemical Society.
2.3.2 Synthesis of Anisotropic Nanocrystals

The morphology of nanocrystals can be further manipulated by controlling the monomer concentration (Figure 2-3).\textsuperscript{26-28, 30} The fast nucleation rate and then relatively low monomer concentration will result in the growth of quasi-spherical nanocrystals (quantum dots), since the growth rate for every crystal facet is slow and relatively the same due to low monomer concentration. However, anisotropic nanocrystal growth requires much higher monomer concentration with a kinetic growth mechanism. Since the crystal growth rate exponentially depends on the surface energy of crystal facets; at a high monomer concentration and in a kinetic growth regime, the facets with higher energy will grow much faster than those with lower energy, resulting in the anisotropic crystals such as rods, tetrapods, disks, etc.\textsuperscript{28, 53, 54} In term of CdSe nanocrystals, the high incoming flux of monomers will diffuse to the nuclei sphere that will be mainly consumed by the c-axis of the CdSe nanocrystals.

The selective adhesion of surfactants on crystal facets is also an important approach to control the anisotropic growth of nanocrystals. The mechanism is that the surface energy of the certain facets will be lowered when surfactants selectively adhere to them and then the growth rate of these facets will be decreased or even prohibited. Alkylphosphonic acids, which usually exist as impurities in technical grade TOPO, have firstly and so far largely been chosen as surfactants for growing anisotropic CdSe nanocrystals.\textsuperscript{28} These PA molecules preferentially bind to the Cd-rich (01\textbar 10) and (11\textbar 20) facets, which are often the side facets of nanorods.\textsuperscript{55} The strength for selective adhesion of PA molecules is also related to the length of alkyl chain, which could direct the growth of anisotropic nanostructures.
2.4 Surface Chemistry

Nanocrystals have a very high surface-to-volume atom ratio, over 50% of the atoms are located on the surface for a 2 nm quantum dot. Such a high surface-to-volume atom ratio leads to a strong domination of the properties of colloidal nanocrystals and also a significant influence on the application. In general, a weak coordinating ligand (or non-coordinating ligand) and a strong coordinating ligand will both be used during synthesis. The weak or non-coordinating ligand typically serves as solvent and controls the reactivity of the monomer; while the strong coordinating ligand reacts with metal precursors to form metal-ligand complex and participates in nanocrystal growth by selectively binding to crystal planes.

The surface ligands in nanocrystal surface can be generally classified as L-type ligands and X-type ligands. The L-type ligands (weak or non-coordinating ligands) are neutral molecules binding to nanocrystal surface by donating a lone pair of electrons and forming a dative bond. TOPO, TOP, TOPSe, and alkylamine are typical L-type ligands.

Figure 2-4. (color) Schematic illustration of a colloidal nanocrystal containing both an inorganic core and an organic ligand shell. A layer of cation is also absorbed to the inorganic core surface. The organic shell layer contains both neutral L-type ligands and charged X-type ligands.
ligands. The X-type ligands (strong coordinating ligands) are negatively-charged molecules that could ionically or covalently bond to the cation-rich nanocrystal surface. The typical X-type ligands include alkylphosphonic acids such as TDPA and alkylcarboxylic acid such as oleic acid and stearic acid. The qualitative and quantitative identifications of these surface ligands can be performed by Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), X-ray photoelectron spectroscopy (XPS), etc.\textsuperscript{58}

Due to the dynamic equilibrium nature of nanocrystal – ligand interaction, the surface chemistry of colloidal nanocrystals can be readily tailored through ligand-exchange and removal. The exchange or removal of ligands from the nanocrystal surface is related to the binding strength between nanocrystal and ligands, the steric hindrance of the ligands, and the ligand – solvent interaction.\textsuperscript{18} Post-syntheses purification (dispersing in good solvent and precipitating with poor solvent) is usually employed to remove the unbound ligands or dissociated ligands in the incubated solution. It also liberates some weakly-bonded ligands from the nanocrystal surface either in the form of free ligands or metal-ligand complexes. Ligand-exchange with short chain molecules such as butylamine or pyridine is the other typical protocol to remove the L-type ligands.\textsuperscript{59} Nonetheless, the ionic or covalent bonding nature of the X-type ligands makes them much more difficult to remove by standard purification methods or exchanged with amine-based molecules. The alternative approach to repel these X-type ligands is by using small molecules with strong nucleophilic groups such as EDT, etc.\textsuperscript{60} Finally, when exposed to the air, nanocrystal surface is also very vulnerable to
oxidation, resulting in liberation of metal-ligand complexes or pure ligands and simultaneous formation of “insulating” metal oxides.

2.5 Optical and Electronic Properties

2.5.1 Optical Properties

Unlike their bulk crystal and small molecule counterparts, colloidal nanocrystals exhibit unique optical properties governed by the chemical composition, size, structure, and surface properties.\(^{20, 25, 38, 44}\) Absorption of a photon with energy higher than the band gap energy leads to the excitation of a valence electron to the CB. This electronic transition is subjected to the selection rule: the wave vector \(K\) should be conserved before and after transition. The \(K\) is automatically conserved for the direct semiconductor for this transition, while a phonon is required for the indirect semiconductor. Note that the \(K\) values have also been quantized for the finite nanocrystal size.

The optical absorption of colloidal nanocrystals can be readily tailored by varying size without changing chemical composition. CdSe nanocrystals, for example, exhibits absorption across the entire visible range by varying the size from 7 nm to 4 nm (Figure 2-5).\(^{25, 61}\) Due to the discrete energy levels of the quantum dots, the absorption edges corresponding to the heavy hole, light hole and split-orbital transitions for bulk CdSe disappeared; instead, a number of absorption features appeared (Figure 2-1), which are due to the \(nS_h-1S_e\) and \(nP_h-1P_e\) transitions.\(^{62, 63}\) For instance, the first two absorption edges for 5 nm CdSe nanocrystals can be assigned to the \(1S_{2/3}-1S_e\) and \(2S_{3/2}-1S_e\) transitions, the third to the \(1P_{3/2}-1P_e\) transition, and others to the higher energy level transitions (Figure 2-5). In addition, the quantum confinement effect, which leads to the drastic overlapping of wave functions of the charge carriers, also results in
a significant increase in the absorption coefficient (or oscillator strength) as the nanocrystal size decreases.\textsuperscript{38} In a practical viewpoint, such high absorption coefficient makes nanocrystals potential candidates as building block for photovoltaic devices with ultra-thin light-absorbing layers.\textsuperscript{64}

Multi-exciton generation (MEG) or carrier multiplication is a phenomenon that generates two or more excitons by absorbing one photon with energy at least twice the band gap of the nanocrystal.\textsuperscript{65-67} The excited electron may release its excess kinetic energy to excite another electron from HOMO level in a collision-like Auger process, resulting in generation of a bi-exciton or multi-exciton and an internal quantum efficiency (IQE) over 100%. This phenomenon has been observed in some nanocrystal systems such as PbS and PbSe, with over 100% external quantum efficiency (EQE) being observed recently for a PbSe quantum dots solar cell.\textsuperscript{68}

![Figure 2-5](image_url)

Figure 2-5. (color) Optical properties of colloidal CdSe nanocrystals with different sizes. The inset indicates the absorption and emission processes of colloidal nanocrystals interacting with incident photons.
Emission, reverse process of absorption, is also dependent on nanocrystal size and surface property. As shown in Figure 2-5, the excited electron in the higher energy level could relax to the lowest energy level and then recombine with the hole in the ground state; the excess energy for this recombination will be released either as heat for non-radiative recombination or as a photon for radiative recombination. The electron relaxation process is well demonstrated by the fact that the emission spectrum is very narrow (typical full width with half maximum, FWHM, ~20-30 nm) and becomes longer compared to the absorption spectrum (Figure 2-5). The recombination process is rather complicated and varies in different categories of nanocrystals and surface properties.

Some nanocrystals can capture one type of charge carrier in the shallow traps at the nanocrystal surface and the recombination process is achieved by capture of the other oppositely-charged carrier; whereas most nanocrystals that have much higher energy levels confine electron and hole within the finite nanocrystal, thus the emission process happens when the wave functions of electron and hole overlap to a desired degree.\textsuperscript{26, 62} The size-dependent emission is typically reflected in the emission spectrum at the band edge; while in some cases, the other emission bands appear at higher energy levels resulting from intraband recombination due to the surface defects.

Surface passivation with inorganic shells has been introduced to reduce surface defects or traps that could potentially damage the quantum yield of quantum dots. Apart from this, an inorganic shell with wider energy gap also further confines the exciton within the nanocrystal, thus increasing the possibility of radiative recombination. This concept has been demonstrated in a variety of nanocrystal systems through successive ion layer adsorption and reaction (SILAR)\textsuperscript{69} as well as non-epitaxial growth\textsuperscript{70}. The shell
layer can be deposited layer-by-layer and the overall nanocrystals maintain monodispersity. Type-II quantum dots with staggered VBs and CBs between the core and shell materials, firstly demonstrated by Bawendi and co-workers, provide another approach to engineer the wave functions between electron and holes.\textsuperscript{71} For example, CdTe-CdSe core-shell quantum dots having a VB maximum in CdTe while a CB minimum in CdSe could separately confine the hole in the VB of CdTe and electron in the CB of CdSe. Carrier recombination occurs across the interface between the core and the shell. Recently Nie and co-worker demonstrated by tuning the lattice strain between core and shell materials with type-II band alignment, the core-shell nanocrystals not only preserve high photoluminescence yield but also can tune the emission spectrum.\textsuperscript{72} Hence, the emissive wavelength is feasible to be tuned by varying the thicknesses of the core and shell layers, and even emissive photon energy lower than the lowest bulk bandgap of core and shell materials can be achieved.

\subsection*{2.5.2 Electronic Properties}

The electronic properties of colloidal nanocrystals are, to a large extent, molecule-like and dominated by the surface properties. The charge transport properties (carrier mobility and type) of colloidal nanocrystals in solid thin film state can be measured by time-of-flight (TOF), carrier extraction by linearly increasing voltage (CELIV), field-effect transistors (FETs), and space charge limited current (SCLC), etc.\textsuperscript{44} Though there is some deviation between different methods, in general, it follows the similar order of magnitude and trends. The carrier density and lifetime of QD thin films can be determined by capacitance-voltage (C-V) analysis and transient photovoltaic measurement, respectively.
Colloidal nanocrystals have been regarded as electronically-isolated “artificial” atoms, because the organic monolayers physically isolate the nanocrystals and separate electronic interaction with the adjacent counterparts.\textsuperscript{36} An effective approach to accomplish the electronic exchange between nanocrystals is by replacing the long-chain organic monolayers with short-chain small molecules. Exchanging the TOPO-capped CdSe nanocrystals with pyridine, for example, leads to two-to-three orders of magnitude increase in electron mobility, reaching $10^{-4} - 10^{-6}$ cm$^2$·V$^{-1}$·s$^{-1}$ depending on the nanocrystal size.\textsuperscript{73} Treating nanocrystals with bidentate molecules such as ethanedithiol (EDT) or benzenedithiol (BDT) further shortens the contact distance between nanocrystals and leads to the enhancement in carrier mobility to $\sim10^{-4} - 10^{-6}$ cm$^2$·V$^{-1}$·s$^{-1}$ for the demonstrated nanocrystals such as CdSe, PbS, PbSe, etc.\textsuperscript{74,75} Talapin et al. treated the PbSe nanoparticle thin films with hydrazine to further decrease the interparticle spacing and increase the electronic coupling.\textsuperscript{76} They found that the electron and hole mobilities of the PbSe nanoparticle thin films can be as high as 0.9 and 0.2 cm$^2$·V$^{-1}$·s$^{-1}$, respectively; and the transport of the carrier type can be switched by varying the treating conditions. Furthermore, passivating with inorganic molecular chalcogenide complexes (MCCs) brings the transport property of colloidal nanocrystals to a level similar to amorphous Si, with $\mu_e \sim 16$ cm$^2$·V$^{-1}$·s$^{-1}$ obtained for CdSe quantum dots passivated with In$_2$Se$_4$\textsuperscript{2-}.\textsuperscript{77,78}

The charge transport among colloidal nanocrystals has been considered mainly through hopping and tunneling. The hopping behavior can be described by the early models proposed by Mott, Efros and Shklovskii.\textsuperscript{79-82} The Mott hopping model primarily describes the conduction in a disordered system, and illustrates that the hopping
probability is determined collectively by the energy difference ($\Delta E_{ij}$) between charge localized site ($E_i$) and a nearby site ($E_j$) and the spatial distance ($r_{ij}$). When the hopping between the nearest neighboring sites dominates at low temperature, deviated from Arrhenius behavior, the temperature-dependent conductivity can be expressed as

$$\sigma \propto \exp\left[-\left(\frac{T_0}{T}\right)^{1} \right]$$

(2-3)

where $T_0 = e^2/\alpha \varepsilon$, $\alpha$ is the localization length and $\varepsilon$ the dielectric constant. For depicting the hopping conductivity other than the nearest sites, the expression can be changed to $T^{-1/4}$ dependence.

The Efros-Shklovskii hopping model assumes that the quantum localization length is much smaller than the spatial distance between hopping sites, thus the temperature dependence of conductivity is given by

$$\sigma \propto \exp\left[-\left(\frac{T_0}{T}\right)^{1/2} \right]$$

(2-4)

If $\Delta E_{ij}$ is equal to or smaller than the Coulomb gap ($\Delta$), the Efros-Shklovskii mechanism can be changed to the Mott model. This Coulomb gap is around twice the energy required to remove one charge from the particle, and can be approximated as $e^2/(2\pi \varepsilon r)$ for a quantum dot with a radius $r$.

The coupling energy $\beta$ between the two neighboring particles that determines the tunneling probability can be approximated as

$$\beta \approx h \times \exp(-2\pi \Delta x \sqrt{\frac{8m^*\Delta E}{h^2}})$$

(2-5)

where $h$ is Planck’s constant and the second term is the tunneling rate, $m^*$ the effective mass of the charge carriers, and $\Delta E$ and $\Delta x$ are the height and width of the tunneling barrier, respectively. Apparently, the coupling energy and tunneling rate increase
exponentially as the $\Delta x$ decreases. This has been experimentally demonstrated in several systems of colloidal QDs that decreasing the interparticle distance sharply increases the electrical conductivity. As mentioned, exchanging long-alkyl-chain molecule on the nanocystal surface with short-chain molecules or small molecules is the typical means to decrease the interparticle distance ($r_{ij}$ and $\Delta x$) and thus improve the electrical transport.

2.6 Application in Photonic Energy Conversion Devices

2.6.1 Quantum Dot Photovoltaic Cells

Quantum dot photovoltaic (PV) cells have rapidly emerged as a potential new technology recently. The advantages inherent from colloidal quantum dots for PV application include the compatibility with a variety of low-cost wet chemistry processing techniques and flexible substrates, readily customized absorption to match the solar spectrum, potentially efficient MEG, etc. PbS and PbSe have large bulk Bohr radii that offers great opportunity to tune the absorption coverage by varying their sizes. The QD PV cells were pioneered based on PbS and PbSe QDs as light-harvesting materials and with a structure of QDs sandwiched by two electrodes, as shown in Figure 2-6a. The QDs were built up layer-by-layer with a thickness of several hundred nanometers to 1 micrometer upon a transparent ITO electrode that forms Ohmic contact with the QDs for Schottky solar cells; and each QD layer was treated with EDT or BDT to remove the bulky organic ligands. A low work-function metal electrode (Al, Ag, Ca, etc.) was then vacuum-deposited on the top of QDs to complete device fabrication.

Upon illumination, the p-type light-absorbing QD layer generates excitons and subsequently dissociates into free electron and hole under the assistance of built-in potential. The p-type QDs have a Fermi-level close to that of the transparent electrode
and band-bending is not necessary for the extraction of hole from QD layer; while the low work-function metal has $> 0.5$ V difference in work function that produces a band-bending in the QD – metal interface. Such band-bending favors the electron extraction and also provides an energetic barrier for hole transport. The asymmetric electrodes provide a built-in potential that could sweep out the charge carriers in the entire depletion regions. In order to fully extract the photogenerated charge carriers, high electron and hole mobilities are essential, particularly for the minority carrier. For p-type QDs, the depletion region is typically ranging from 100 – 150 nm, thus the minority carrier electrons generated in the neutral region and close to the ITO side need to overcome the long traveling distance (nearly the whole QD layer thickness) to reach the metal electrode. Despite high EQE that has been achieved for QD PV cells in the visible region, the EQE in the near-infrared region is still low ($< 20\%$), which is mainly due to the low absorption coefficient ($\alpha \sim 10^{-4} \text{ cm}^{-1}$) in this region.\textsuperscript{64} Increasing the QD layer thickness to $\sim 1\mu\text{m}$ could lead to $> 90\%$ absorption in the near-infrared, while the charge carrier (minority carrier) is not likely to escape such a thick film before recombination.
occurs. To address this absorption – extraction compromise requires higher carrier mobility, better design of device architecture, and more efficient removal/passivation of QD defects.\textsuperscript{84} To date, by tailoring the QD size and composition and engineering device architecture, $\eta_p$ of 3-5\% has been reported for these Schottky-type QD PV cells by several independent groups.\textsuperscript{64, 68, 74, 75, 84, 85}

Sargent and co-workers recently introduced depleted heterojunction concept for QD PV cells, where QDs were built up on the top of $\text{TiO}_x$ pre-coated upon a fluorine-doped tin oxide (FTO) substrate (Figure 2-6b).\textsuperscript{86} These depleted heterojunction PV cells have the advantages that the minority carriers can separate more efficiently since charge generation occurs at the illuminated electron-accepting $\text{TiO}_x$ side. Together with improved atomic passivation of colloidal QDs, $\eta_p \sim 6\%$ has been achieved for depleted heterojunction QD PV cells recently.\textsuperscript{87} Moreover, MEG has also been realized in PbSe QD solar cells with dual EDT and hydrazine treatment during QD layer building-up, resulting in significant contribution to photocurrent generation with peak EQE $\sim 114\%$.\textsuperscript{68} However, in order to transform this technology to real commercialization, further improvement in $\eta_p$ is a must, which again relies on the better understanding of both device physics and chemistry/material science of colloidal quantum dots.

2.6.2 Quantum Dot Light-Emitting Diodes

Solution-processed electroluminescent quantum dot light-emitting diodes (QD-LEDs) with multi-layer structure are another example of optoelectronic application of colloidal nanocrystals (Figure 2-7). The high color purity and photophysical stability of quantum dots together with their compatibility with roll-to-roll processing are the potential advantages to explore this technology. QD-LEDs have a typical structure of transparent electrode (ITO) / hole transporting layer (HTL) / QD emissive layer / electron
transporting layer (ETL) / reflective cathode (Al) (Figure 2-7). The basic operation mechanism is the injected electron and hole from corresponding electrodes recombine at the QD layer with photon emission.

The efficiency of a QD-LED is directly related to the PL quantum efficiency of quantum dots. The organic-monolayer-protected quantum dots are vulnerable to external stimuli that lead to the instability of QDs and thus the unreliability of quantum efficiency. Coating with an inorganic shell layer upon the quantum dots is the typical approach to engineer QDs. The type-I core-shell structure such as CdSe/CdS and CdSe/ZnS not only enhances the physical stability but also increases the radiative recombination efficiency by confining charge carriers within the core. Though they are more prone to non-radiative recombination due to the separate location of electron and hole, the type-II core-shell QDs such as CdTe/CdSe have also been intensively studied to tune the emission wavelength from visible to near-infrared regime. The high-efficiency QD-LEDs are typically fabricated using core-shell QDs nowadays.
The HTL and ETL have been introduced to balance the hole and electron injection and increase the LED efficiency. The typical HTL materials include poly(N, N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine) (PolyTPD), PEDOT:PSS, poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)-diphenylamine) (TFB), NiO, MoO$_3$, WO$_3$, etc.; and Alq$_3$, ZnO, TiO$_x$, etc. have been usually used as ETL materials in QD-LEDs. The energy level, mobility, carrier concentrations (inorganic), and processing conditions of HTL and ETL materials are the parameters affecting the LED performance. Also, blending or interfacing QDs with hole-transporting polymers as hole-transporting and emissive layer has also been investigated. Exploring HTLs with high work function to directly inject holes into QDs is still a challenge. In addition, though QD-LEDs with a solution-processed ZnO or TiO$_x$ layer have shown much improvement in efficiency and lifetime, the accompanied Auger-process also leads to loss of a large amount of charge carriers.

QD-LEDs have witnessed great progress in the past decade, with EQE ~1% for blue, ~10% for green, and ~20% for red at brightness ~100 – 1000 cd/m$^2$ achieved. Further advance as a commercial interest requires not only the increase in device performance by finely tailoring quantum dots and HTL and ETL materials and optimizing device architecture but also the development of economical processing in current QD-LEDs.
CHAPTER 3
INTRODUCTION TO ORGANIC ELECTRONIC MATERIALS AND DEVICES

3.1 Introduction

This chapter introduces a class of molecular solids that hold together through weak van der Waals interaction. These molecular solids are typical organic materials primarily composed of carbon and hydrogen atoms. The atoms that form the molecules are bounded together through strong covalent interaction, while the intermolecular interaction is mainly van der Waals interaction (molecular interaction). The fact that the organic solids have strong intramolecular interaction but weak intermolecular interaction results in drastic difference in the optical, electronic, and mechanical properties compared to the inorganic counterparts and also offer great opportunity to broaden their application to a wide range through economical wet chemistry processing methods.

In general, organic materials can be classified as discreted small molecules, polymers, and biological molecules (Figure 3-1a). The polymers and biological molecules are macromolecules with molecular weight in the range of 10 000 g/mol to several millions Da. Polymers have molecular-weight and structure polydispersities and strictly speaking, are not chemically-pure; biological molecules have the most complex structures but are chemically-exclusive (Figure 3-1a). This dissertation focuses on organic semiconducting materials that have electrical conductivity in between metals and insulators. Both small molecules and natural/synthetic conjugated polymers can be organic semiconductors; though some biological molecules such as deoxyribonucleic acid (DNA) have ever been studied in optoelectronic devices, these materials are neither classified as the organic semiconductors nor the study of interest here.
The weak intermolecular interaction and good affinity with organic solvents make organic materials dissolvable in solution that makes them compatible with solution processing methods for thin film deposition. Furthermore, the weak intermolecular interaction also results in good mechanical ductility of organic materials that can be flexibly shaped to follow the supporting substrates. In addition, the modern synthetic chemistry enables the development of thousands of new small molecules and polymers.
with customized properties every day, as shown in Figure 3-2. Hence, all of these intrinsic and extrinsic properties offer great potential to manufacture large-area, cheap and flexible organic optoelectronic devices.

In fact, organic semiconductors have fueled much interest both in academia and in industry since the pioneer work by Tang who first demonstrated a simple bilayer heterojunction organic solar cell with $\eta_p$ exceeding 1% in 1986$^{13}$ and successively a bilayer heterojunction organic LED exhibiting 1% quantum efficiency in 1987 together with VanSlyke.$^{89}$ After that, Friend and co-workers demonstrated the first LED made using conjugated polymers in 1990.$^{90}$ Today, organic LED (OLED) has already went into market as displays in cell phone, jumbo-size TV, etc.; and small-area state-of-the-art organic photovoltaic cells (OPVs) fabricated in laboratory exhibit $\eta_p$~10%,$^4$ approaching the commercial needs (Figure 3-3). Certainly, the application of organic semiconductors is not limited to OLED and OPVs, many other devices such as field-effect transistors (FETs),$^{91}$ photodetectors,$^{14}$ and sensors have also been developed using both small molecules and polymers (Figure 3-3).

The study of organic semiconductors can be traced back to 1960s and a vast amount of documentary literatures on this field have been published from then on.$^{88, 92}$

![Organic LED TV](image1.jpg)  ![Organic solar cells](image2.jpg)  ![Organic transistors](image3.jpg)

Figure 3-3. (color) Optoelectronic devices made using conjugated organics as active /responsive materials.
Thus, this chapter will only go through some basic knowledge of organic electronic materials and devices that provides as a context for the coming work. In particular, photovoltaic cells based on organics and organic-inorganic hybrids will be strengthened, which is the theme of this dissertation.

3.2 Electronic Structure and Properties of Organic Semiconductors

3.2.1 Atomic Orbital Hybridization and Bonding

The bonding nature of carbon atom governs the properties of the organics. The electronic configuration of the carbon atom at the ground state is 1s^22s^22p^2. There are four valence electrons in the outer electronic level, with two electrons paired in the 2s orbital and the other two unpaired in the 2p orbital. The outer 2s and three 2p orbitals may mix to create a set of equivalent degenerate orbitals and relocate the four electrons unpaired. This orbital mixing can be occurred to 2s orbital with one, two, or all three 2p orbitals to create sp, sp^2, or sp^3 hybridization, respectively (Figure 3-4). Before hybridization, only the unpaired two electrons in the p orbitals could share with other atoms to form covalent bonds; and hybridization makes all the valence electrons available for bonding. Though a slight increase in the total energy of the carbon atom is
required after hybridization, this energy increase can be compensated by the energy released during bond formation.

As mentioned earlier in chapter 2, when two atoms approach each other, the atomic orbitals interact to form bonding MOs and anti-bonding MOs. The bonds formed between s, p, and sp\(^n\) orbitals are called \(\sigma\)-bond, and the bonds formed by overlapping two \(p_z\) orbitals are named \(\pi\)-bond. Benzene, for example, has 2s and two 2p orbitals hybridized, resulting in three sp\(^2\) hybridization orbitals and one unaltered 2p\(_z\) orbital. The \(\pi\)-bond in benzene is perpendicular to the plane containing all the carbon atoms and creates a delocalized electron density above and below the carbon-atom plane; on the contrary, the sp\(^2\) orbitals generates localized electron density in the ring plane and between carbon and hydrogen atoms. Such an alternation of a single bond (\(\sigma\)-bond) and a double bond (a \(\sigma\)-bond and a \(\pi\)-bond) between the carbon atoms in benzene is the basis of the conjugated organics that exhibit favorable electronic property. Furthermore, the \(\sigma\)-bond is stronger than \(\pi\)-bond for the larger orbital overlapping. Thus, the energy levels of the bonding \(\pi\) and anti-bonding \(\pi^*\) MOs are in between the bonding \(\sigma\) and anti-bonding \(\sigma^*\) MOs.

Despite the bonding among atoms within an organic molecule is covalent \((E_{\text{cov}}=2-4 \text{ eV})\), the intermolecular bonding is typically weak van der Waals interaction \((E_{\text{vdW}}=10^{-3}-10^{-2} \text{ eV})\). Thus, the electronic structure and property of organic solids are, to a large extent, molecule-like. Nonetheless, since the energy of the van der Waals interaction varies with distance \((r)\) given as following:

\[
U_{\text{vdW}} \propto r^{-6}
\]  

(3-1)
the molecular orientation and packing could significantly influence the electronic properties in solid state. When the molecular orbitals considerably overlap as two molecules approach each other, the repulsive component of dispersion force becomes significant. This repulsion is also distance dependent; and the potential energy rising from both this contribution and intermolecular attraction is typically described by Lennard-Jones potential:

\[
U(r) = U_{\text{attr}}(r) + U_{\text{rep}}(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}]
\]

where \(\varepsilon\) and \(\sigma\) are constants.

This weak intermolecular interaction endows organic molecules/solids with unique properties. Apart from good affinity with organic solvents and mechanical ductility, organic semiconductors typically have much lower charge carrier mobility (10\(^{-6}\) – 1 cm\(^2\)r\(-1\)V\(-1\)s\(^{-1}\)) than inorganic counterparts. Furthermore, excitons generated in organic solids are strongly bounded in the nearby molecules, rather than rapidly dissociated and delocalized within the whole solid.

### 3.2.2 Excitons in Organic Solids

#### 3.2.2.1 Exciton types

Similar to the inorganic semiconductors, the interaction of organic solids with light leads to promoting an electron from a HOMO to an empty LUMO and simultaneously leaving a positive hole in the HOMO. The photogenerated electron and hole are not free particles in the respective energy level, but bounded as a neutral electron-hole pair or called exciton. The excitons can be generally classified to three types based on the difference in binding energy to the original molecule: Frenkel, charge-transfer, and Wannier-Mott (Figure 3-4). As shown in Figure 3-5, Wannier-Mott exciton is usually
present in inorganic semiconductors for the high dielectric constant and strong atomic interaction. Its Coulombic binding energy is a few meV and Bohr radius on the order of 10 nm. Due to the low dielectric constant and weak intermolecular interaction, the exciton generated in organic solids is typically Frenkel. The facts that the binding energy can be as high as 0.1-1 eV\textsuperscript{94,95} but the Bohr radius is only on the order of 1 nm make Frenkel exciton highly localized on the molecule. Charge-transfer exciton delocalizes to a few molecules, which occurs in solids with long-range order or as an intermediate process during exciton dissociation in either donor-acceptor interface or organic-based devices.

### 3.2.2.2 Exciton Properties

Excitons can be formed by optical excitation or free electron and hole recombination in organic solids. The binding energy of excitons is mainly contributed from the Coulombic, electron-lattice and electron-electron interactions. This binding energy should be overcome if excitons want to dissociate into free charge carriers.

Figure 3-5. (color) Schematic illustration of three types of excitons in a solid. (a). a Frenkel exciton, localized within a single molecule; (b). a charge-transfer exciton, slightly delocalized to two or a few adjacent molecules; (c). a Wannier-Mott exciton, highly delocalized with radius much greater than the lattice constant \(a_L\).
Other than binding energy, exciton diffusion length and lifetime are other important parameters in organic-based electronic devices.

The behavior of the exciton (generation and recombination) involves a series of optical transitions that also determines the absorption and emission properties of the organic solids. Though the transitions between energy states contain several energetic processes such as electronic, vibrational and rotational processes, only the electronic transition has the energies the same as those of near-infrared, visible and ultra-violet photons that are of interest for optoelectronic device application. Hence, electronic transition will be only considered for the study of exciton behavior in organic solids here.

Jablonski energy diagram, shown in in Figure 3-6, summarizes a series of optical and electronic transitions that exciton can undergo in organic semiconductors. The generated exciton by optical absorption has a singlet type due to spin conservation and a series of radiative and non-radiative transition will follow. The possibility of these transitions, according to the selection rule, is dependent on the time scale. The exciton can relax to dissipate energy such as undergoing vibrational relaxation or internal conversion with conserved spin state; and can also further absorb photonic energy that may lead to transitions to higher energy levels such as from $S_1$ to $S_2$, etc. Exciton may also undergo intersystem crossing when the vibrational levels of the two excited states overlap, resulting in the change of spin state.

Exciton generated by recombination of a free electron with a free hole has lower energy state than the free electron due to its binding energy. Since the spin state of electron is not restricted by that of hole during this recombination process, the generated exciton could be either singlet or triplet (the theoretical permutation ratio of
The singlet exciton can relax to the singlet ground state accompanying with emission of a photon or fluorescence; and the triplet exciton can also relax to the singlet ground state in a molecule with allowed intersystem crossing, resulting in phosphorescence. Since phosphorescence involves a spin-orbital coupling process, its time scale (0.1-1 ms) is much longer than that of fluorescence (1-100 ps). Both of fluorescence and phosphorescence have much longer lifetime than that of vibrational transition (0.1 ps). Hence, the exciton thermally relaxes to the lowest excited state before undergoing photon emission processes, leading to red-shift in emission spectrum in organic semiconductors. This shift can also be explained by the Frank-Condon effect, which demonstrates photon emission requires an emission of a phonon due to the coordination coordinate shift between the ground state and the excited state, thus resulting in lowering in photon emission energy. Other than radiative processes, there are also a number of non-radiative processes that an exciton in organic solids may carry on, as shown in Figure 3-6.

Figure 3-6. (color) Jablonski energy diagram. The radiative transitions and non-radiative transitions are indicated by squiggly arrows and straight arrows, respectively. Adapted from www.olympusmicro.com.
3.2.2.3 Exciton Motion

The motion of the excitons in organic solids can be described using the thermally-activated hopping model. The exciton transport is important to understand the mechanism and optimization of organic-based optoelectronic devices. Several mechanisms have been proposed to describe the exciton motion including energy transfer and energy migration.

First, cascade or trivial energy transfer is a process of reabsorption of a photon emitted from a donor molecule by an acceptor molecule\(^8\). This energy transfer is important at long distances and when there is strong overlap between the donor emission and acceptor absorption spectra. Furthermore, this process also leads to lengthen the apparent lifetime of the singlet state.

The second mechanism is Förster energy transfer, which, similar to cascade energy transfer, also depends on the spectrum overlap between the donor emission and acceptor absorption. The energy received by the acceptor from the donor can be transferred to the degenerate states and subsequently relaxed to vibronic states of low energy, which produces a dephasing of the excited state and also vibrational decay. In a very-weak coupling limit with \(\Delta E > |J|\) (\(\Delta E\) represents the vibrational bandwidth of the acceptor electronic state and \(J\) is the strength of the interaction between the donor and the acceptor), the transfer rate by the assumption that the transfer of electronic excitation energy between a donor and an acceptor is mediated by dipole-dipole interaction can be written as\(^8\)

\[
K_{D \rightarrow A} = \frac{1}{r_D^6} \frac{1}{R^6} \frac{3}{4\pi} \int \frac{e^4}{\omega^4 n_0^4} F_D(\omega) n_A(\omega) d\omega
\]

(3-3)
where $F_D(\omega)$ is the normalized fluorescence emission spectrum, $\sigma_A(\omega)$ is the normalized acceptor absorption cross section, $n_0$ is the refraction index of the solvent, $c$ is the speed of the light, $\tau_D$ is the natural lifetime of the donor, and $\omega$ integration is over all the frequencies. Hence, it is straightforward that the transfer is not occurred unless there is overlap between $F_D(\omega)$ and $\sigma_A(\omega)$.

Dexter extended the theory of resonance energy transfer to exciton states with electron-exchange between donor and acceptor. This transfer distance is very short (~1nm), but it is of importance in the case of triplet-triplet energy transfer. The transfer rate is given by \(^{(3-4)}\)

$$K_{D\rightarrow A} = \frac{2\pi}{\hbar} |\beta_{DA}|^2 \int F_D(E)F_A(E)dE$$

where $\beta_{DA}$ is the exchange energy interaction between molecules, $F_D(E)$ and $F_A(E)$ are the normalized phosphorescence spectrum of the donor and absorption spectrum of the acceptor molecule, respectively.

Due to the non-directional nature of these energy transfer processes, the exciton migration can be approximated as random hopping diffusion. Thus, Fick's second law of diffusion can be used to describe the exciton migration with time

$$\frac{\partial \varphi(r)}{\partial t} = D \frac{\partial^2 \varphi(r)}{\partial r^2}$$

(3-5)

where $\varphi(r)$ the concentration of the excitons and $D$ is the diffusion coefficient.

Diffusion length ($l$), a distance that an exciton can travel before relaxing back to the ground state, is related to the diffusion coefficient and exciton lifetime and given by

$$l = \sqrt{ZD\tau}$$

where $Z=6$, $4$, and $2$ for three, two, and one dimensions, respectively. The
diffusion length for organic semiconductors is typically 5-20 nm, as experimentally
determined by methods such as luminescence quenching.\textsuperscript{14, 97}

3.3 Charge Transport in Organic Solids

The charge transport of solids can be very different depending on the bonding
nature and intermolecular interaction. Inorganic crystals that hold together through
strong covalent or ionic bonding lead to the strong overlapping of atomic orbitals in
three dimensions and then the formation of transport band. The charge transport can be
highly delocalized in this band that is slightly affected by the present impurities, defects,
and phonon scattering. However, molecular solids that hold together through weak van
der Waals interaction exhibit much more complicated transport behavior. Charge carrier
mobility in organic solids can be influenced by a number of internal and external factors
such as molecular packing, impurities, molecular weight and distribution, disorder,
temperature, pressure, electric field, etc.\textsuperscript{98-100} The angle-dependent charge carrier
mobility of pentacene single crystal is an example of molecular packing.\textsuperscript{88}

In inorganic solids, charge transport is mainly governed by the electronic
interaction, and the electron-phonon interaction is very small that is considered as a
perturbation. However, in molecular crystals, the electron-phonon interactions are
comparable to or even larger than the electronic interaction, which leads to the
formation of polaron, quasiparticle of phonon-dressed electronic charge.\textsuperscript{99}

Organic crystals with long range order at low temperature may exhibit band-like
transport behavior. A slightly delocalized transport energy band can be formed in
organic solids with high structural regularity, resulting in maximum carrier mobility \( \geq 1 \)
cm\(^2\) V\(^{-1}\) s\(^{-1}\) at room temperature.\textsuperscript{88} This band-like transport is subjected to the
environmental temperature as $\mu(T) \propto T^{-n}$, ($n > 1$), and this temperature dependence attributes to the large electron-phonon interaction in molecular solids.

In fact, most of the organic solids are morphologically amorphous due to their bonding nature. Hopping model is mostly popular for describing the transport behavior of injected charge carrier within organic solids. The typical motion of highly localized polaron in amorphous organic solids is characterized by hopping from site to site and scattered as a result of interaction with the local environment. The mobility in term of electric field and temperature then can be expressed as

$$\mu(F, T) \propto \exp\left(\frac{-\Delta E}{kT}\right) \cdot \exp\left(\frac{\beta \sqrt{F}}{kT}\right)$$  \hspace{1cm} (3-6)

where $F$ is the electric field, $\Delta E$ is the activation energy for intermolecular hopping, and $\beta$ is a constant.

The mobility of charge carrier in molecular solids can be determined by time-of-flight, field-effect transistors, space-charge-limited-current, etc. Time-of-flight is typically used for thick films (>1μm) and the structural defects can be reflected in the resultant mobility. FETs method has been favored for organic crystals, while mobility determined by FETs is highly sensitive to the organic-electrode and organic-dielectric contact preparation, the surface polarity, dielectric topology, etc. SCLC offers a convenient means to determine the mobility from the electrical characteristics of diodes with organic layer sandwiched by two electrodes. This method is particularly useful for ultrathin films (tens to hundreds of nanometers). The charge injection is determined by the choice of electrodes and only one type of charge carriers can be extracted for the chosen electrodes. Ideally, for organic thin film with traps, $J - V$ curves may exhibit several regions: i). a linear regime where the transport is injection-limited, ii). an
intermediate region, iii). an SCLC region where \( J \) scales quadratically with applied voltage, iv). a trap charge limited conduction (TCLC) region where \( J \) scales cubically with \( V \), and v). a trap-free SCLC regime. In the first SCLC regime, the \( J-V \) characteristics can be expressed by Child’s law as\(^\text{88, 103}\)

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}
\]

(3-7)

where \( L \) is the film thickness, \( \varepsilon_r \) is the dielectric constant, and \( \mu \) is the charge carrier mobility.

### 3.4 Organic Photovoltaic Cells

#### 3.4.1 Principle of Organic Photovoltaic Cells

Unlike the conventional inorganic PV cells, the operation mechanism of organic-based PV cells including all-organic and organic-inorganic hybrid solar cells are based on donor-acceptor (DA) heterojunction formed between two different materials with staggering energy levels.\(^\text{13, 14}\) As shown in Figure 3-7, the incident photons can be absorbed by the donor and acceptor materials, leading to the generation of a tightly-bound exciton.\(^\text{88, 104-106}\) The photogenerated exciton then diffuses to the DA hetero-interface with sufficient energy difference for dissociation.\(^\text{104}\) However, the binding energy rising from the electron-hole mutual Coulomb attraction is sufficiently high (0.3-1 eV) due to the low dielectric constant of organic materials (\( \varepsilon_r: \sim 2-4 \)), thus the energy offsets between the LUMOs of the donor and the acceptor or/and between the HOMOs of the donor and the acceptor should be higher than this binding energy for achieving exciton dissociation into free electron and hole (polarons) at the DA interface. The dissociated free polarons are then collected by the respective electrodes.
The absorption efficiency ($\eta_A$) depends on the absorption coefficients of the donor and acceptor materials and their collective thickness.\textsuperscript{106} The exciton diffusion efficiency ($\eta_{ED}$) depends on the exciton diffusion length and the degree of phase separation.\textsuperscript{107,108} Uniform and delicate phase-separation is essential for efficient exciton diffusion in organic-based PV cells.\textsuperscript{108,109} Through careful control in donor and acceptor materials processing, phase separation with an ideal size (around twice of the exciton diffusion length) is achievable in bulk-heterojunction (BHJ) PV cells.\textsuperscript{110} For example, as shown in Figure 3-8, hybrid film based on polymer and CdSe nanocrystals (~ 6-7 nm) shows well separated binary phases with phase size ~10 nm, around the twice of the exciton diffusion length.\textsuperscript{61} In contrast, exciton diffusion is the major limiting factor in bilayer-heterojunction PV cells.\textsuperscript{14}

The exciton dissociation (charge transfer) process is not straightforward, but rather complicated with a series of competitive sub-processes involved.\textsuperscript{111} A number of emerging studies indicate that charge-transfer state is of critical importance in both photocurrent generation and open-circuit voltage ($V_{oc}$) in organic solar cells.\textsuperscript{111-114} When
exciton diffuses to the DA interface, the initial step may generate an interfacial charge-transfer (CT) state (Figure 3-9). This initial hot CT state will thermalize with an increased electron-hole separation distance. Germinate recombination (GR) may occur in the singlet state ($S_0$) at the relaxed CT state.\(^\text{111}\) Besides, the relaxed CT state can undergo rapid spin-mixing between its singlet and triplet states, which could result in the transfer from the singlet state to the triplet state ($T_1$). Otherwise, the CT state can undergo full charge separation into free positive and negative polarons. According to the Onsager theory,\(^\text{115}\) the efficiency of exciton dissociation is critically dependent upon the thermalization length and Coulomb capture radius. In the viewpoint of kinetics in exciton dissociation, the steps between thermalization and charge-transfer and between GR and charge-separation (CS) are regarded as the main competitive processes. Due to the ultrafast nature of charge transfer,\(^\text{116}\) the typical charge transfer efficiency for bulk-heterojunction PV cells based on conjugated polymers /small molecules and fullerene derivatives is close to unity; while this efficiency is still under debate for BHJ.
Figure 3-9. (color) Energy level diagram of the possible main processes of exciton dissociation in an organic-based PV cell. CT: charge-transfer; CS: charge-separation; GR: germinate recombination; and BR: bimolecular recombination.

polymer:nanocrystal hybrid PV cells due to the complex nanocrystal surface / interface. However, the GR during exciton dissociation has been independently demonstrated to be related to the device’s $V_{oc}$. Thus, managing the GR is essential in achieving both unity $\eta_{CT}$ and high $V_{oc}$.

Charge carrier transport, the final step of photocurrent generation, also critically relies on the active layer morphology (Figure 3-8) and the donor and acceptor mobilities. The highly percolated network of the donor and acceptor materials has been regarded as the ideal morphology for efficient charge transport. The phase separation in polymer:nanocrystal hybrids, as shown in Figure 3-8, is in a degree of ~10 nm. Such a delicate separation is of advantage for efficient exciton diffusion; while it may be too fine to carrier transport due to the possible wavefunction overlapping of electron and hole. This overlapping may lead to an increased bimolecular recombination, which, to a large extent, accounts for the loss of photocurrent in organic-based PV cells. Addressing this exciton diffusion – charge transport compromise rising
from the donor-acceptor phase separation is of great importance for high-efficiency BHJ PV cells.

Thus, the external quantum efficiency (EQE or \( \eta_{\text{EQE}} \)) that is defined as the ratio of the number of collected electrons to the number of incident photons is the multiplication of the efficiencies of each process and expressed by \( \eta_{\text{EQE}} = \eta_A \eta_{\text{ED}} \eta_{\text{CT}} \eta_{\text{CC}} = \eta_A \eta_{\text{IQE}} \), (Figure 3-7).

### 3.4.2 Progress of Organic Photovoltaic Cells

Organic PV cells have witnessed drastic progress during the last decade with \( \eta_p \) reaching 10% recently.\(^4\) Organic PV cells have been typically classified as small molecule (SM) and polymer PV cells. The SM PV cells utilize organic small molecules as donor and fullerene (C\(_{60}\) or C\(_{70}\)) as acceptor. Though SM PV cells using solution processing have shown some significant progress recently,\(^{117}\) the high crystallinity of small molecules together with unfavored phase separation make high-vacuum thermal evaporation technique still the primary choice.\(^{14}\) Polymer solar cells (PSCs) are using conjugated polymers as donor and fullerene derivatives as acceptor and based on bulk-heterojunction structure.\(^{107}\) The PSCs are fabricated from solution by spin-coating, dip-coating, even roll-to-roll, etc. There are many similarities in the research of small molecule and polymer solar cells; here we emphasize the latter with a brief progress overview.

The ultrafast energy transfer from a conjugated polymer to C\(_{61}\)-butyric acid methyl ester (PC\(_{61}\)BM) observed independently by Heeger and Yoshino and their coworkers in early 1990s is the basis of the development of BHJ polymer solar cells.\(^{116,118}\) Though the planar-structured PSCs was firstly demonstrated in 1993\(^{119}\), this structure suffers from inefficient exciton dissociation and charge carrier transport, which
received little attention after introduction of bulk heterojunction concept. BHJ PSCs were pioneered by Heeger and co-workers by blending poly(2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene) (MEH-PPV) and PC\textsubscript{61}BM. BHJ PSCs have then shown dramatic progress by tailoring conjugated polymers and fullerene derivatives, optimizing the active layer morphology, and engineering the device structure.

### 3.4.2.1 Conjugated polymers

Though MEH-PPV was firstly developed for the BHJ polymer solar cells, poly(3-hexyl thiophene) (P3HT) has then shown to play a leading role due to its wider absorption coverage, higher molecular regioregularity, and correspondingly higher hole mobility.\textsuperscript{107,120-122} Partly due to the vast commercial availability, good air stability and facile processing, P3HT:PC\textsubscript{61}BM blend has become the standard system for testing new device architecture and studying device physics.\textsuperscript{123} The \(\eta_p\) of P3HT:PCBM cells falls within the range of 2-5%.\textsuperscript{123} However, the relative large energy gaps of PPV and PT derivatives make PSCs fabricated using these materials only absorb small part of solar photons, leading to relatively low \(J_{sc}\) (~12 mA/cm\(^2\)).\textsuperscript{123}

To harvest a large portion of the near-infrared (NIR) solar photons, a series of low-gap polymers have been developed in the past several years. One of the common basic designing rules for the low-gap polymers is to co-polymerize an electron-donating unit with an electron-accepting unit. This copolymerization leads to the energy level overlapping of the electron-donating unit molecule and electron-accepting unit molecule, resulting in raising HOMO level, lowering LUMO level and thus lowering the energy gap.\textsuperscript{124} Poly(2,1,3-benzothiadiazole-4,7-diyl(4,4-bis(2-ethylhexyl)-4H-cyclopenta(2,1-b:3,4-b')) dithiophene-2,6-diyl)) (PCPDTB) is the first low-gap copolymer developed based on this design rule for PSCs with \(\eta_p >3\%\) and with significant harvesting of NIR
photons. The unending endeavor in developing semiconducting copolymers by a number of research groups lead to the numerous reports of PSCs based on the blends of these copolymers and PCBM with $J_{sc}$ in the range of 12-16 mA/cm$^2$. Apart from narrowing the bandgap, the mobility, intermolecular interaction, and molecular chain packing of polymers can also significantly affect $J_{sc}$. Finally, it is worth mentioning that replacing C$_{60}$ with C$_{70}$ in PCBM typically results in 10% increasing in $J_{sc}$ due to better absorption of the latter.

For these state-of-the-art cells based on low-gap polymers, though the $J_{sc}$ reaches 15 mA/cm$^2$, the $V_{oc}$ is still not high enough (< 0.7 V), partly because the energy level alignment between polymer donor and fullerene acceptor is not optimized. Leclerc and co-workers then developed poly((9-(1-octynonyl)-9H-carbazole-2,7-diyl)-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl) (PCDTBT) with HOMO level of 5.5 eV, ~0.3-0.4 eV lower than P3HT and PCPDTBT. Such deep HOMO can be of great benefit to increase the $V_{oc}$ of PSCs using model acceptor PCBM, since empirically the $V_{oc}$ follow the equation:

$$V_{oc} = (\frac{|E_{HOMO}^{donor} - |E_{LUMO}^{acceptor}|}{e} - 0.3)V$$

High $V_{oc}$ (0.9V) was indeed obtained for PSCs based on blends of PCDTBT and PC$_{71}$BM.

3.4.2.2 Morphology

Delicate phase separation of donor and acceptor blends is of critical importance for BHJ organic solar cells. Morphology control is usually achieved by thermal and solvent annealing for PSCs using conjugated polymers and fullerene derivatives. For example, P3HT:PCBM film casted from dichlorobenzene after slow solvent annealing
results in higher electron and hole mobilities, more balanced charge transport and better absorption.\textsuperscript{121} Similarly, higher crystallinity and better phase separation have also been observed in P3HT:PCBM with thermal annealing.\textsuperscript{133,134} Thus, the $\eta_P$ of PSCs based on P3HT:PCBM with improved morphology after either solvent or thermal annealing reaches to 4-5%, around 1-2 times higher than control devices without any treatment.

Although thermal and solvent annealing are very effective in P3HT:PCBM cells, these methods are not as effective as in PSCs based on low-gap polymers such as PCPDTBT.\textsuperscript{126} Bazan and co-workers discovered that processing PCPDTBT:PCBM blends using dichlorobenzene mixing with some additives such as alkanedithiol could result in better morphology favored for exciton diffusion and charge carrier extraction, and thus the significant increase in $J_{sc}$ from 10 mA/cm$^2$ to 16 mA/cm$^2$ and in $\eta_P$ from 3.5% to 5.5%.\textsuperscript{135} This discovery has then been extensively extended to a variety of materials system with better morphology.

3.4.2.3 Device architecture

The basic device structure of organic solar cells is the active layer sandwiched by a transparent electrode such as ITO and a reflecting electrode such as Al and Ag. PEDOT:PSS has typically used as anode interlayer to smooth the ITO surface and accordingly increase work function. Moreover, transition metal oxides such as MoO$_3$, WO$_3$, NiO, and V$_2$O$_5$ have also been developed as anode interlayer with comparable device performance.\textsuperscript{136,137} On the other hand, LiF,\textsuperscript{138} TiO$_x$,\textsuperscript{128} and ZnO,\textsuperscript{139} either processed by vacuum deposition or solution casting have usually introduced between the active layer and the cathode to improve the performance of PSCs. The high transparency makes TiO$_x$ and ZnO promising to tune the optical field distribution within the active layer.
Moreover, the transparent and conductive metal oxides are also applicable as inter-connecting layer for solution-processed multi-junction solar cells. Multi-junction solar cells have the advantages of absorbing solar photons in each junction with selective wavelengths and simultaneously adding the voltages produced in each junction. Due to relative large bandgap of organic materials, making PSCs with multi-junction could be of exceptional benefit. The early example by Kim et al. demonstrated a tandem cell with PCPDTBT:PCBM as front cell (the cell close to transparent electrode) to absorb NIR photons and P3HT:PCBM as back cell (the cell close to the reflective electrode) to harvest visible photons. The cell showed open-circuit voltage addition of two subcells and $\eta_p$ as high as 6.5%, even close to the efficiency addition of the two single-junction PCPDTBT:PCBM cell (3.0%) and P3HT:PCBM cell (4.7%).
CHAPTER 4
EFFECT OF COLLOIDAL NANOCRYSTALS ON HYBRID PHOTOVOLTAIC CELLS

4.1 Introduction

Progress in synthetic chemistry of inorganic materials enables us to tailor nanocrystals with variable size, shape, composition, and surface chemistry.\textsuperscript{27} For example, the emissive property, which can be manipulated by engineering nanocrystal size and shape, makes colloidal nanocrystals rising star emitters in light-emitting diodes\textsuperscript{32} and biological labeling/imaging.\textsuperscript{34, 35} Colloidal nanocrystals that not only have been regarded to inherit the intrinsic properties (high electron mobility and environmental stability) of their bulk counterparts but also possess "molecule-like" solution-processability were introduced into polymer photovoltaic cells as electron acceptor.\textsuperscript{16}

The main roles of the colloidal nanocrystals in hybrid PV cells are photogeneration (light absorption, or exciton generation), charge transfer by creating a donor-acceptor junction with organic material, and electron transport. With these in mind, recently, it is a trend to study organic-inorganic hybrid or quantum dot PV cells by tailoring colloidal nanocrystals with defined chemical, electronic, and morphological structures.\textsuperscript{18, 84}

In this chapter, we attempt to understand the effect of chemical composition, size, shape, and even surface chemistry of colloidal nanocrystals on the performance of hybrid PV cells. The electronic structure of the colloidal nanocrystals will be also probed to relate with the performance of the hybrid PV cells.
4.2 Colloidal Nanocrystals Synthesis and Processing

4.2.1 Spherical Nanoparticles Synthesis

Spherical CdSe nanoparticles (or quantum dots) were synthesized according to the reported method with some modification.\textsuperscript{61,142} 76 mg CdO (Alfa Aesar), 3 mL oleic acid (Sigma-Aldrich), and 3.0 g trioctylphosphine oxide (Sigma-Aldrich) were mixed and heated to 280 °C under N\textsubscript{2} flow. A 1.0 mL trioctylphosphine (Sigma-Aldrich) solution containing 78 mg Se (Sigma-Aldrich) was injected at 280 °C. The reaction mixture was kept for 1–5 min at 270–290 °C to produce CdSe nanoparticles with average sizes of 4–7 nm. The reaction was then terminated by adding 5 mL toluene into the mixture. CdSe nanoparticles were purified by precipitation with methanol and re-dissolution in toluene for three cycles.

CdS quantum dots were synthesized as follows.\textsuperscript{143} CdO (154 mg), OA (3 mL), and ODE (45 mL) were mixed and heated to 250 °C under N\textsubscript{2} flow, at which temperature S/ODE (38 mg/6 mL) was injected. Aliquots were taken for monitoring the nanocrystal size. After reaction, the solution was naturally cooled to R.T., and purified by methanol precipitation and hexane dispersion.

4.2.2 Nanorods Synthesis

CdS nanorods were synthesized according to the published method.\textsuperscript{144} CdO (0.105 g), octadecylphosphonic acid (ODPA, 0.45 g), and TOPO (1.45 g) were mixed and heated to 320 °C under N\textsubscript{2} flow until a clear mixture solution obtained. The mixture was then cooled to 120 °C and pumped for 1 h at this temperature before re-heating to 320 °C, at which point 1 mL TOP was injected. After the temperature returned to 320 °C, the S/TOP (120 mg/1.5 mL) mixture was injected and the reaction was kept at 310–320 °C for 85 min. The mixture was naturally cooled to room temperature, and 5 mL...
toluene was added. Cd$_x$Se$_{1-x}$ nanorods were synthesized the same as CdS nanorods, with the exception of S/Se/TOP injection (85 mg S/0.3 mL TBP/0.5 mL TOP; 15 mg Se/0.15 mL TBP/0.5 mL TOP/ 0.3 mL toluene).

CdSe nanorods were synthesized in a similar manner as CdS nanorods. CdO (0.205 g), TOPO (3.0 g), and TDPA (0.85 g) were mixed and heated to 320 °C under N$_2$ flow until a clear mixture solution obtained. The mixture was then cooled to room temperature and aged for 24 h, and then re-heated to 320 °C, at which point Se/TBP/TOP/toluene (63 mg/0.3mL/1.0mL/0.3mL) mixture was injected. The reaction was kept at 250 - 280 °C for 40 min, and then was naturally cooled to room temperature. The width and aspect ratio of CdSe nanorods were tuned by varying the growth temperature.

### 4.2.3 Nanocrystal Processing

The purified CdSe nanoparticles (~80 -100 mg) were mixed with 10 mL pyridine and sonicated for 10 min at room temperature. The nanoparticles / pyridine mixtures were then transferred to a three-necked flask and stirred for another 24 h under N$_2$ flow at room temperature. After ligand-exchange, the nanoparticles were precipitated from pyridine solution by hexane. The precipitated nanoparticles were dried in a vacuum oven. Polymer:CdSe hybrid solution was prepared by dispersing 30 mg CdSe nanoparticles and 3 mg of conjugated polymers in chlorobenzene/pyridine (90/10, v/v) co-solvent.

CdS and CdSe nanorods were purified by precipitation with methanol and dispersing in toluene for 6 cycles. The purified nanorods were mixed with 5 – 10 mL pyridine and refluxed for 24 h. Then the nanorods were collected by hexane precipitation. In order to completely remove the exchanged alkyl-chain ligands, the
pyridine-exchanged nanorods were re-dissolved in toluene and then centrifuged to collect the nanorod solids. Finally, the nanorods were dried and re-dispersed in chloroform before mixing with conjugated polymers with a concentration of 30 mg nanorods and 3 mg polymers for characterization and device fabrication.

4.3 Hybrid Film Characterization and PV Cell Fabrication

4.3.1 Nanocrystals and Hybrid Film Characterization

The purified CdSe nanoparticles and nanorods were characterized using a JEM-2010F transmission electron microscope (TEM) and a JEOL 200CX TEM both with a 200 keV electron beam energy. UV-Vis absorption was recorded on a Cary UV-Vis absorption spectrometer. The X-ray diffraction (XRD) was carried out in an X’Pert powder X-ray diffractometer. The surface morphology of the hybrid thin films was characterized using a Veeco Nanoscope atomic force microscopy (AFM) operated in tapping mode.

4.3.2 Hybrid PV Cell Fabrication

Glass substrates pre-patterned with indium tin oxide as anode (ITO) ($R_s$: 20 Ω/□) were cleaned by successive sonication with soap, deionized water, acetone, and isopropanol for 15 min, followed by exposure to UV-ozone for 15 min. A poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS, Clevious P, H.C.Stark) layer was first spin-coated on the ITO substrates and annealed in air at 150 °C for 15 min. P3HT:CdSe hybrid active layer was spin-coated in a N₂ glove box with H₂O and O₂ both < 0.1 ppm and then annealed at 150 °C for 30 min. For devices based on nanorods, the active layers were processed from chloroform and annealed at 120 °C for 20 min. The devices were completed by vacuum deposition of an Al cathode through a shadow mask, resulting in each device with an active device area of approximately 4
mm². The PV devices were characterized by $J-V$ measurement under dark and 1 sun AM 1.5G illumination. The EQE measurement was performed as described in Chapter 1.

4.4 Nanocrystal Characterization and Properties

4.4.1 Nanocrystal Size

CdSe nanoparticles with different size were synthesized, as shown in Figure 4-1. The 4 nm particles are almost monodisperse and self-assembled into hexagonal structure in carbon-coated copper grid. When the sizes increased to ~5 nm and 6 nm, the nanoparticles become less monodisperse; while further increasing nanoparticle size by prolonging reaction time results in significant size defocusing and presence of both spherical particles and elongated rods (Figure 4-1d). The difference in size dispersity is likely due to monomer consumption.⁴³ The initial monomer concentration and precursor injection temperature control the concentration of nuclei. The growth, to a large extent, is also monomer-concentration-dependent. At high monomer concentration, the monomer diffusion to each nucleus is higher than the consumption rate, resulting in monodispersity; however, as the monomer consumed, the monomer reaching each particle becomes unequal, which leads to the size polydispersity. Ostwald growth will appear as the monomer is further consumed to a threshold, which leads to the dissolution of small particles (particles with high surface energy) and the growth of large particles, as shown in Figure 4-1d.

UV-Vis absorption spectra of the CdSe nanocrystals were shown in Figure 4-2. The first excitonic peaks of all four samples are apparent, while they become less pronounced as nanocrystal size increases, another indication of size polydispersity. Due to the quantum confinement effect, as the nanoparticle size decreases, the
Figure 4-1. TEM images of CdSe NPs with different sizes: (a) 4.0 nm, (b) 5.0 nm, (c) 6.1 nm, and (d) 6.8 nm. The scale bars are 20 nm.

absorption blue-shifts and the corresponding band gap increases. The estimated band gaps of these nanocrystals, based on the absorption onset, are in the range of 1.8 eV (6.8 nm) - 2.0 eV (4.0 nm). The broadening in band gap as nanoparticle size decreases also leads to the corresponding shift in the CB and VB of the nanocrystals. The magnitude of the change in CB and VB is related to the effective mass of electron and hole of the bulk materials, respectively. Both band gap and energy level changes should be carefully taken into account once the nanocrystals are used as the active materials in optoelectronic devices.

4.4.2 Nanocrystal Shape and Composition

Nanocrystal shape and composition, another two important parameters determining the nanocrystal properties, can be tailored in a simultaneous manner. Using facet-defining organic surfactants such as alkyl phosphonic acids, elongated nanorods,
Figure 4-2. (color) UV-Vis absorption spectra of CdSe nanoparticles with different sizes. Rather than quantum dots can be achieved. Figure 4-3 shows TEM images of CdS, CdS$_x$Se$_{1-x}$, and CdSe nanorods passivated by alkylphosphonic acids. The width and aspect ratio of these nanorods can be readily controlled by varying monomer concentration, reaction time and temperature, and surfactant type. For example, nanorods synthesized using longer alkyl chains have shorter width and higher aspect ratio, which is likely due to the steric hindrance effect of the long alkyl chains, resulting in less favored side growth. Increasing the growth temperature can result in short and fat nanorods, suggesting growth favored along the side direction. This may be due to the increasing kinetic energy for ligand-attachment and ligand-detachment, and also the more uniform monomer distribution along the nanocrystal head and side. Finally, branched nanocrystals have frequently appeared in nanorod synthesis, which is likely due to the impurity of alkylphosphonic acids and the present of zinc-blende CdSe nanoparticles at the initial growth stage (Figure 4-3).

Though elongated nanocrystals may have dimension in one direction much larger than their Bohr radius, the quantum confinement effect is more or less conserved.
Figure 4-3. TEM images of composition-varied semiconductor nanorods: (a) CdS, width:3.1 nm, A.R. ~30; (b) CdS$_{x}$Se$_{1-x}$, width: 3.2 nm, A. R. ~21; (c) CdSe, width:4.0, A. R. ~ 10. The scale bars for (a, b): 100 nm, and (c): 50 nm.

compared to the spherical nanoparticles with size similar to their width.\textsuperscript{146,149} The absorption spectra of nanorods, shown in Figure 4-4, exhibit characteristic and size-dependent absorption properties. For example, CdS nanorods show a very sharp first excitonic absorption peak and pronounced second absorption peak with a band gap of ~2.6 eV. The band gap of the nanocrystals can also be readily tuned by changing the nanorod composition. For example, if S and Se precursors are co-injected into Cd precursor solution, ternary nanorods CdS$_{x}$Se$_{1-x}$ can be produced. The recent study by Ruberu \textit{et al.} demonstrated that CdSe would grow first due to the higher reactivity of Se/TOP and the resulting nanocrystals are partly alloyed with non-uniform rod-like structure.\textsuperscript{147} In this case, the nanorods are very uniform, though further study is needed for the composition distribution in these ternary nanorods. The nanorods also show a red-shift in absorption compared to pure CdS nanorods, yet the excitonic peaks become less pronounced, partly due to the non-uniform distribution of CdSe and CdS components. In addition, pure CdSe nanorods show defined absorption spectrum with a band gap of 1.9 eV (Figure 4-4).
Figure 4-4. (color) UV-Vis absorption spectra of composition-tunable semiconductor nanorods.

X-ray diffraction is employed to further characterize these nanorods. As shown in Figure 4-5, all nanorods show characteristic peaks of wurtzite phase and peak broadening due to the finite dimension. $\text{CdS}_x \text{Se}_{1-x}$ nanorods shows defined diffraction peaks locating in between those of CdS and CdSe nanorods, suggesting partial alloy of S and Se. Based on Vegard’s law, the composition of the alloyed nanorods can be estimated as $\text{CdS}_{0.34} \text{Se}_{0.66}$.

The nanocrystal surface is also of critical importance for understanding its growth and properties and for optoelectronic devices and biomedical application. However, it is not straightforward to quantitatively identify the nanocrystal surface due to its complicated nature rising from synthesis and crystallization, the characterization techniques including optical and electrical measurements typically reveal the collective properties of the nanocrystals rather than individual particle. Since this dissertation focuses on the application of colloidal nanocrystals in photovoltaic cells, here we will not particularly discuss the nanocrystal surface yet will definitely connect nanocrystal surface when the nanocrystals become a dominant factor of device performance.
Figure 4-5. (color) XRD patterns of composition-tunable Cd-chalcogenide nanorods.

4.5 Effect of Device Aging on Performance

We began this study in the P3HT:CdSe hybrid PV cells, partly because this system is more mature in processing and device fabrication. Though the previous study indicated hybrid PV cells based on spherical nanoparticles were not efficient (< 1%), the advancement in nanocrystal synthesis makes them worthwhile to re-visit as acceptor in hybrid PV cells.

An abnormal aging behavior has been observed for the unencapsulated P3HT:CdSe hybrid PV cells when exposed to air. As shown in Figure 4-6a, the initial test showed high dark current and small rectification ratio at \(1/-1\) V (~60), while the dark current was decreased and rectification ratio increased to ~450 after exposing to the air for 0.5 h. Though the dark current was further decreased after 2 h exposure, the rectification ratio also decreased to ~18 due to the reducing in forward current. The \(J-V\) characteristics under 1 sun AM 1.5G illumination show corresponding behaviors. First, low \(J_{sc} = 3.2\ mA/cm^2\) and \(V_{oc} = 0.42\ V\) were exhibited under initial test. After exposure to the air for 0.5 h, both \(J_{sc}\) and \(V_{oc}\) were drastically increased to 4.7 mA/cm\(^2\).
and 0.68 V, respectively, resulting in the increase of $\eta_p$ from initial 0.6% to 1.5%. The device performance can be maintained at this stage for $\sim$ 0.5 – 1 h, and varied due to the difference in sample preparation. After 2 h exposure, however, the $J_{sc}$ was decreased to the initial level (3.0 mA/cm$^2$) and $\eta_p$ was dropped to < 0.5% due to the drastic decrease in FF and subsequent increase in series resistance (from initial 3.0 $\Omega \cdot cm^2$ to 202 $\Omega \cdot cm^2$)

This aging behavior has also been observed in hybrid PV cells based on CdSe nanorods. As shown in Figure 3-6b, the dark current decreased when exposed to air for a period of time and simultaneously the rectification ratio increased. Similarly, the device showed low $J_{sc}$ and $V_{oc}$ at the initial test, and then gradually increased. The

![Diagram](a) CdSe quantum dots

![Diagram](b) CdSe nanorods

Figure 4-6. (color) Aging effect of hybrid PV cells based on colloidal nanocrystals. $J$ - $V$ characteristics of hybrid PV cells based on P3HT and CdSe quantum dots (a) or nanorods (b) under dark and 1 sun AM 1.5G solar illumination.
maximum device performance was observed after exposure to the air for 5 h and retained at this level for several hours. After 24 h, the device efficiency was dropped to less than half of the best value due to the large decrease in $V_{oc}$. The increase in $V_{oc}$ can be mainly explained by the decrease in dark current as exposed to the air, since the $V_{oc}$ is the voltage at which the dark current equals to the photocurrent and a reduced dark current requires a higher voltage with equal photocurrent. However, the change in $J_{sc}$ and FF is less understood at this moment.

In order to rule out the potential influence of post-fabrication relaxation of the hybrid films, we tested the devices that had been kept at a N$_2$-filled glove box for 12 h. These devices exhibited the similar initial aging behavior as exposed to the air as the freshly-prepared devices. Further study indicates that this aging behavior also occurs in hybrid PV devices using other conjugated polymers such as PCPDTBT (Chapter 7), in the devices with a ZnO NP layer (Chapter 5 and Chapter 6), and in the devices with resin encapsulation as well. This behavior has seldom appeared in all-organic P3HT:PCBM PV cells. Together, we attribute this phenomenon to the interaction of CdSe nanocrystals with water / oxygen.

Air-induced photoluminescence enhancement was observed in several colloidal nanocrystal systems.$^{150-155}$ The early study by Koberling et al.$^{151}$ showed the exposure of CdSe nanocrystals to the oxygen changes both the intensity and fluctuation of photoluminescence, which is likely due to the injection of electrons to the oxygen via an Auger process, leaving a positively-charged nanocrystal. The air-induced fluorescence also occurred in CdSe/ZnS core-shell nanocrystals. Muller et al.$^{153}$ proposed that the neutralization of charged non-emissive nanocrystals by oxygen adsorption facilitated by
the presence of water is the mechanism of this air-induced fluorescence enhancement. The study by Cordero et al.\textsuperscript{150} showed water molecules are responsible for the increased luminescence intensity of CdSe nanocrystals. The initial adsorption of water molecules passivates the CdSe nanocrystal surface and leads to the enhancement of the luminescence, while the extended exposure to air leads to the formation of an oxide layer that consequently results in luminescence quenching. The observation by Pechstedt et al.\textsuperscript{155} further demonstrated that photoinduced fluorescence enhancement of CdSe/ZnS nanocrystals requires the involvement of water molecules while only the presence of oxygen leads to the generation of non-emissive nanocrystals due to the photoinduced electron transfer to the oxygen.

Hence, these studies give much insight on revealing the abnormal aging effect of hybrid PV cells based on CdSe nanocrystals. The exposure of the devices to air leads to the adsorption of oxygen and water molecules to the CdSe nanocrystal surface. In a limited period of time, this adsorption passivates the dangling bond of the nanocrystal surface and reduces the density of surface defects. In other words, this reduces exciton and/or charge carrier recombination as reflected by the increase in $J_{sc}$ and $V_{oc}$. Further exposure could lead to the formation of an oxide layer in the nanocrystal surface, resulting in the transition of a semiconductor to a quasi-insulator and thus the huge increase in nanocrystal resistance, as reflected in the drastic decrease in $J_{sc}$ and/or FF of hybrid PV cells (Figure 4--6).

4.6 Effect of Nanocrystal Size on Device Performance

The optical and electronic properties of colloidal nanocrystals are size-dependent due to the quantum confinement effect, which motivates us to study the effect of nanocrystal size on the performance of hybrid PV cells. The $J$ – $V$ characteristics of
hybrid PV cells based on CdSe nanocrystals with different sizes are shown in Figure 4-7a. The device based on 4 nm CdSe shows $J_{sc} = 1.5 \text{ mA/cm}^2$ and $V_{oc} = 0.81 \text{ V}$. As the nanoparticle size increases from 4 nm to ~ 7 nm, the $J_{sc}$ increases accordingly yet $V_{oc}$ decreases slightly. The plot shown in Figure 4-7b indicates a quasi-linear relationship between $J_{sc}$ and nanoparticle size. Since the size dependence of $V_{oc}$ is not as significant as $J_{sc}$, $\eta_p$ follows the same size-dependent trend as $J_{sc}$ (Figure 4-7b). The maximum efficiency of the hybrid PV cells using P3HT and ~ 7 nm spherical CdSe particles is 1.9±0.2%, which is, to our knowledge, one of the highest efficiency reported based on the P3HT:CdSe system. We endeavored to further increase the nanoparticle size to achieve higher device performance. Unfortunately, this attempt was unsuccessful due to the difficulty in dispersing large particles (size > 8 nm) in organic co-solvents.

The wavelength-dependent EQE of hybrid PV cells based on P3HT and CdSe

![Figure 4-7. (color) Nanocrystal size effect: $J$-$V$ characteristics (a) of hybrid PV devices based on CdSe nanoparticles and P3HT and the corresponding plots of short-circuit current density ($J_{sc}$) and power conversion efficiency ($\eta_p$) versus nanocrystal size (b).](image-url)
nanoparticles with different size is shown in Figure 4-8. The device using 6.8 nm particles shows significantly higher EQE than the 4.0 nm device, which is consistent with $J – V$ measurement. Besides, the EQE of the 6.8 nm device is red-shifted slightly compared to the 4.0 nm device due to its lower band gap. Furthermore, the 6.8 nm device shows the highest EQE of 42%, about three times higher than that of the 4.0 nm device.

Figure 4-8. (color) EQE of P3HT:CdSe hybrid PV devices based on different nanoparticle sizes.

Though larger nanoparticles slightly extend the absorption, the significantly higher EQE of the device with larger nanoparticles indicates that other electronic processes are the determining factors. We then measured electron mobility of P3HT:CdSe hybrid films with different nanoparticle size following the SCLC method. The electron-only device has a structure of P3HT:CdSe hybrid film sandwiched by Al. Hence, the electron mobility is attained by fitting the $J – V$ characteristics shown in Figure 4-9 according to the Child’s law (eq. 3-7, $\varepsilon_r = 6.5$ and $L = 100$ nm). Thus, the electron mobilities ($\mu_e$) of hybrid films with 4.0 nm and 6.8 nm CdSe particles are $(6 \pm 2) \times$
and (5±2) × 10⁻⁵ cm²V⁻¹s⁻¹, respectively. Improvement in electron mobility in hybrid thin film can be of great benefit in the extraction of photogenerated charge carrier. Plus, the improved electron mobility is more balanced with hole mobility (1×10⁻⁴ cm²V⁻¹s⁻¹) of P3HT in hybrid system, which is also reflected in the increase in FF for the 6.8 nm device. Furthermore, nanoparticles with larger size have less surface atoms and thus less surface defect density. These surface defects could act as recombination centers for photogenerated excitons and charge carriers, resulting in lower photocurrent for the device with small nanoparticles. Thus, the improved electron mobility together with less surface defect density lead to the enhanced $J_{sc}$ and $\eta_p$ for the devices based on large nanoparticles. Finally, the fact that the slight decrease in $V_{oc}$ as size increases could attribute to the decrease in energy offset between polymer HOMO and nanocrystal CB due to the decrease in nanocrystal band gap.

![Figure 4-9](image_url)

**Figure 4-9.** (color) $J$ - $V$ characteristics of electron-only devices with a structure of Al/P3HT:CdSe/Al based on different CdSe NP sizes. The solid lines are fitted curves based on Child’s law.
4.7 Effect of Nanocrystal Shape on Device Performance

The early study by Hyunh et al.\textsuperscript{16} showed that the nanocrystal shape has a pronounced influence on the performance of hybrid PV cells. Nanocrystals with elongated shape may provide direct charge transport pathway and facilitate charge carrier collection. We prepared CdSe nanorods with different width and aspect ratio for hybrid PV cells. The $J-V$ characteristics of the hybrid PV cells using different nanorods were shown in Figure 3-10a. As a comparison, PV cell using CdSe nanoparticles with size comparable to the nanorod width shows $J_{sc} = 4.2$ mA/cm$^2$, $V_{oc} = 0.60$ V, FF = 0.40, and $\eta_p = 1.0\%$. The cell using CdSe nanorods with width of 6.4 nm and aspect ratio of 2 shows increase $J_{sc} = 4.9$ mA/cm$^2$, $V_{oc} = 0.74$, and $\eta_p = 1.4\%$. The performance of hybrid

![Figure 4-10.](image)

Figure 4-10. (color) Nanocrystal shape effect: $J$-$V$ characteristics (a) and EQE (b) of P3HT:CdSe hybrid PV devices based on different NC shapes.
PV cell has been further increased with $J_{sc} = 5.9$ mA/cm$^2$, $V_{oc} = 0.72$, FF = 0.54, and $\eta_p = 2.3\%$ when nanorods with higher aspect ratio used.

The wavelength-dependent EQE further demonstrates the advantage of nanorods as acceptors in hybrid PV cells (Figure 4-10b). Both the EQE at 500 nm $< \lambda < 600$ nm (mainly corresponding to P3HT absorption) and at $> 600$ nm (mainly corresponding to the nanocrystal absorption) increase as nanorod aspect ratio increases, indicating more balanced charge carrier extraction and particularly better electron extraction as reflected in the higher EQE at the low wavelength range.

**4.8 Other Colloidal Nanocrystals**

CdSe nanocrystals have been mostly studied in hybrid PV devices$^{16}$ including in this dissertation, while bulk CdSe has band gap $\sim 1.7$ eV that limits the harvesting of near-infrared region and is also not environmentally-benign. Other colloidal nanocrystals such as CdS$^{156, 157, 158}$, ZnO$^{159}$, Si$^{160}$, CuInS$^{161}$, PbS$^{83, 162}$, and PbSe have also been developed for photovoltaic application including hybrid PV cells. Here we synthesized some CdS nanocrystals for hybrid PV cells. The $J–V$ characteristics of hybrid P3HT:CdS PV cells are shown in Figure 4-11. The cell based on 3 nm quantum dots shows very limited $J_{sc}$ and $V_{oc}$, resulting in an $\eta_p < 0.1\%$. The cell using CdS nanorods shows improved $J_{sc}$ and $V_{oc}$, resulting in an $\eta_p = 1.3\%$. Further engineering in size, shape, and surface chemistry is needed to improve the device performance based on CdS nanocrystals.

**4.9 Summary**

In this chapter we discuss the synthesis and characterization of colloidal nanocrystals for hybrid PV cells. The abnormal aging effect of hybrid PV cells using CdSe nanocrystals have been observed, which is attributed to the complicated surface
Figure 4-11. (color) Hybrid PV devices based on CdS nanocrystals and P3HT. Both devices were EDT treated before Al deposition (See details in Chapter 7).

chemistry, particularly the interaction between the CdSe nanocrystals and moisture / oxygen. Hybrid PV cells also show nanocrystal-size-dependent performance that is mainly accounted by the increased electron mobility and reduced surface defect density. Furthermore, we demonstrated that nanocrystals with elongated structure could be beneficial for hybrid PV cells, since the nanorods may provide direct charge transport pathways for more efficient charge collection. The results based on both CdSe and CdS show that higher efficiency is indeed observed compared to their spherical counterparts.
CHAPTER 5
SOLUTION-PROCESSED MULTI-FUNCTIONAL ZINC OXIDE NANOPARTICLE CATHODE INTERLAYER

5.1 Introduction

Though photogeneration in bulk heterojunction organic-inorganic hybrid solar cells occurs at the photoactive layers, metal (electrode) – semiconductor (active layer) junction is also of great importance, which affects the charge injection and collection. Operation of bulk heterojunction solar cells requires a pair of electrodes with asymmetric work function to facilitate electron and hole injection/collection. Nonetheless, this results in a common challenge that work function of electrode material is not sufficiently low or not high enough to align with the energy levels of the semiconducting active layer, consequently leading to the loss of photocurrent and voltage. Moreover, the direct contact between electrode and active layer may cause exciton recombination at the electrode-active layer interface.163

Introducing electrode interlayer to physically isolate the contact between electrode and active layer and simultaneously increase (for anode) or decrease (for cathode) work function is a feasible approach to address these issues. This concept was early practiced by depositing a PEDOT:PSS layer upon ITO substrate, which witnessed great success in improving the performance of solution-processed organic-based solar cells. On the other hand, introducing a transparent and semiconducting metal oxide layer to separate the active layer and cathode has also been studied in organic-based solar cells.139,164-166 This chapter focuses on the effect of a solution-processed ZnO nanoparticle (NP) cathode interlayer on the performance of hybrid solar cells. The roles of the ZnO NP layer will be also comprehensively surveyed.
5.2 Synthesis and Characterization of ZnO Nanoparticles

ZnO nanoparticles\textsuperscript{167,168} were synthesized by dropwise addition of a stoichiometric amount of tetramethylammonium hydroxide (TMAH) / ethanol solution into zinc acetate dihydrate / dimethyl sulfoxide (DMSO) solution and stirred at room temperature at the air for 1h. After reaction, the nanoparticles were firstly collected by precipitation in ethyl acetate, and then re-dissolved in ethanol and precipitated by hexane for another twice. The purified nanoparticles were dissolved in ethanol with a concentration of \(~30\ \text{mg/mL.} \) ZnO NPs were dropped on carbon-coated copper grid for TEM measurement. For XRD study, dried ZnO NPs powder was used. The thickness of the ZnO NPs processed from ethanol and deposited upon Si substrates was determined by ellipsometry measurement.

As shown in Figure 5-1a, ZnO nanoparticles are uniformly distributed and have an average size \(~3\ \text{nm} \) with narrow size distribution. The XRD pattern shows that the nanoparticles are crystalline with a wurtzite structure and the peaks are being broadened due to their polycrystallinity and small size (Figure 5-1b).

![Figure 5-1. TEM image (a) and XRD pattern (b) of ZnO nanoparticles synthesized by wet-chemistry method.](image-url)
The device structure and schematic energy level diagram of hybrid solar cells have been shown in Figure 5-2. The fabrication of polymer:CdSe hybrid solar cells is the same as described in Chapter 4. The P3HT:CdSe active layer was spin-coated upon ITO substrates pre-coated with a PEDOT:PSS layer from chlorobenzene/pyridine solution. A ~25 nm thick ZnO NP layer was then spin-coated upon the active layer, following by annealing at 150 °C for 30 min at a glove box. Due to the simplicity in synthesis and processing, CdSe nanoparticles were chosen to exemplify the effect of a ZnO NP layer on the performance of hybrid solar cells. Even using nanoparticles, we demonstrate the power conversion efficiency is comparable to those using anisotropic nanocrystals such as nanorods and tetrapods.\textsuperscript{16, 169-171}

As indicated in the energy level diagram, ZnO has a CB ~ 4.2 eV aligned with both CdSe nanoparticles and Al cathode that enables efficient charge extraction from the active layer, and it has a very deep VB ~7.6 eV that may block back transport of
hole into Al cathode. The large optical gap makes ZnO NPs very transparent for the visible light travel/propagation and limits photogeneration at the ZnO NP layer.

We first demonstrate the effect of a ZnO NP layer on hybrid solar cells using archetypal polymer P3HT and CdSe nanoparticles (5 nm), and the $J-V$ characteristics have been shown in Figure 5-3a and the corresponding performance parameters listed in Table 5-1. The device without a ZnO layer shows $J_{sc} = 2.6$ mA/cm$^2$, $V_{oc} = 0.75$ V, FF = 0.42, and $\eta_p = 0.8\%$; while the insertion of a ZnO NP layer significantly increases $J_{sc}$.

Figure 5-3. (color) Typical $J-V$ characteristics of P3HT:CdSe (5 nm) hybrid PV cells without and with a ZnO NP layer under 1 sun AM 1.5G illumination (a) and their corresponding EQE (b).
(4.4 mA/cm$^2$) and FF(0.47), leading to a relative 87% enhancement in $\eta_p$. The enhancement in $J_{sc}$ is also reflected in EQE, as shown in Figure 5-3b, in which the device with the ZnO layer shows higher EQE at $\lambda \geq 350$ nm. In particular, the EQE of the device with a ZnO layer exhibits a peak at $\lambda = 500$ nm that mainly corresponds to the P3HT absorption, suggesting photogenerated holes have been more efficiently collected.

The performance of hybrid PV cells based on spherical nanoparticles, as demonstrated in chapter 4, is dependent on the size of nanoparticles. Here we further demonstrate the effect of the ZnO NP layer on hybrid PV cells using larger nanoparticles. As shown in Figure 5-4, the inclusion of a ZnO NP layer in hybrid PV

![Image](image.png)

Figure 5-4. (color) Typical $J$–$V$ characteristics of P3HT:CdSe hybrid PV cells without and with a ZnO NP layer and using CdSe nanoparticles (6.8 nm) with mixed spheres and rods under 1 sun AM 1.5G illumination.
cells using 6.8 nm CdSe significantly increases the $J_{sc}$ and FF, leading to $\eta_p$ as high as 2.4% with a relative 50% increase compared to the control device. Such efficiency is comparable to the state-of-the-art hybrid solar cells based on P3HT and CdSe nanorods / tetrapods.$^{16, 167, 168}$

The performance parameters in Table 5-1 indicate that the efficiency enhancement of hybrid PV cells with a ZnO layer is primarily from the increase in $J_{sc}$ and secondarily from FF, while the $V_{oc}$ has been slightly decreased. This $V_{oc}$ decrease is mainly due to the increase in dark current for the ZnO devices (Figure 5-5), and the diode characteristics are more or less maintained. The increase in $J_{sc}$ and FF is a consequence of combinatorial electronic, optical, and morphological effects.

### 5.4 Role of the ZnO NP Layer

We investigate the roles of the ZnO NP layer on hybrid PV cells in the perspective of electronics, optics, and morphology. First, the ZnO NP layer physically eliminates the direct contact between the active layer and the Al, which prevents the

<table>
<thead>
<tr>
<th>Active layer</th>
<th>ZnO</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta_p$ (%)</th>
<th>Enhancement (%)</th>
</tr>
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<tbody>
<tr>
<td>P3HT:CdSe (5 nm)</td>
<td>no</td>
<td>2.6</td>
<td>0.75</td>
<td>0.42</td>
<td>0.8</td>
<td>--</td>
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<tr>
<td></td>
<td>yes</td>
<td>4.4</td>
<td>0.72</td>
<td>0.47</td>
<td>1.5</td>
<td>87</td>
</tr>
<tr>
<td>P3HT:CdSe (5.5 nm)</td>
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<td>4.2</td>
<td>0.75</td>
<td>0.40</td>
<td>1.0</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>5.8</td>
<td>0.61</td>
<td>0.50</td>
<td>1.8</td>
<td>80</td>
</tr>
<tr>
<td>P3HT:CdSe (6.8 nm)</td>
<td>no</td>
<td>5.8</td>
<td>0.64</td>
<td>0.44</td>
<td>1.6</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>6.5</td>
<td>0.70</td>
<td>0.52</td>
<td>2.4</td>
<td>50</td>
</tr>
</tbody>
</table>
direct quenching of photogenerated excitons at the active layer – Al interface and inside the active layer as Al penetrated during vacuum deposition. Second, coating a 25-nm-thick ZnO layer upon P3HT:CdSe hybrid active layer reduces the root-mean-square surface roughness from 9.7 nm to 3.8 nm as shown in Figure 5-6. The smoother surface is anticipated to improve the contact between the active layer and the cathode and thus enhance the collection of photogenerated charge carriers.

Moreover, the transparent nature of ZnO enables to change the optical field distribution of the hybrid active layer, as early demonstrated in organic solar cells using either TiO$_x$ or ZnO. The optical field profiles of the devices without and with a ZnO layer have been calculated based on a transfer-matrix theory. The optical constants for the calculation are determined by ellipsometry measurement. As shown in Figure 5-7, the optical intensity has been re-positioned as a ZnO NP layer included, resulting in higher optical field distribution in the active layer. In particular, this effect is more

![Figure 5-5. (color) Typical J – V characteristics of P3HT:CdSe (5 nm) hybrid PV cells without and with a ZnO NP layer under the dark condition.](image)
significant in the long wavelength regime (500 nm < \lambda < 650 nm), since the peak intensity locates at a distance of ~\lambda/4n from the reflecting cathode due to the optical interference, where n is the refractive index of the hybrid active layer. This optical effect has been reflected in the EQE, which is much higher at \lambda > 400 nm for the device with a ZnO layer (Figure 5-3b). Thus, this optical effect enables to tune the absorption of the active layer to maximize the device photogeneration in both conjugated polymers and CdSe nanoparticles by varying the ZnO layer thickness. In addition, the optical effect slightly shifts the photogeneration zone closer to the cathode, which may be advantageous due to the relatively lower electron mobility (~10^{-5} - 10^{-6} \text{ cm}^2/\text{V·s})\text{61} than the hole mobility (~10^{-4} - 10^{-5} \text{ cm}^2/\text{V·s})\text{121}, thus resulting in more balanced charge collection as reflected in the slight increase in FF.

The deep VB (~7.6 eV) of the ZnO suggests the possible blocking of hole diffusion to the cathode (Figure 5-2). We verify this behavior by measuring the EQE of the devices as a function of applied bias at given wavelengths (Figure 5-8). The EQE of the device without a ZnO layer collected at all the given wavelengths exhibits a transition point (a minimum EQE) at a voltage ~ 0.94 – 0.97V, accompanying with a sharp ~ 180° phase change. As observed in the CuPc:C60 mixed heterojunction solar
Figure 5-7. (color) Optical intensity profiles of P3HT:CdSe hybrid photovoltaic cells. The materials in each layer were labeled accordingly.

cells\textsuperscript{172}, this transition behavior in EQE indicates the reversal of photocurrent direction and the photogenerated holes can freely drift into the cathode at high biases, which may also facilitate the hole diffusion from the active layer to the cathode. Nonetheless, the EQE of the device with a ZnO layer shows a monotonic decrease with the bias yet there is no a sharp phase change observed. As indicated by the CuPc/C60 planar heterojunction solar cells\textsuperscript{172}, this behavior suggests the photocurrent direction is unchanged even at high bias where the direction of the electric field is reversed (from the anode to the cathode) and causes the drift of the hole from the active layer to the...
cathode. The unchanged photocurrent direction is only compensated by a higher magnitude of the hole diffusion from the active layer to the anode, which is achieved by the hole-blocking characteristics of the ZnO NP layer.

Figure 5-8. (color) EQE and the corresponding phase change of P3HT:CdSe hybrid PV cells without (a) and with (b) a ZnO NP layer as a function of applied bias.

5.5 Effect of the ZnO NP Layer on Device Environmental Stability

The chemical and morphological instabilities in organic-based solar cells are a very challenge to move this technology into commercial reality. The presence of chemically-varied surface and interface in colloidal nanocrystals against the environment further deteriorates this concern. The study in abnormal aging effect in Chapter 4 exemplifies the influence of the environment on the performance of the hybrid solar cells. This is truly the case for the unencapsulated devices without a ZnO layer, which typically degrades after exposure to the air for hours. Nonetheless, the inclusion of a ZnO NP layer, though the spherical nanoparticles may not pack in a closest fashion, does drastically improve the device stability without any encapsulation when stored at an environment with humidity 35-60% and temperature 21-24 °C. As shown in Figure 5-9, after > 2 months’ storage, both the $J_{sc}$ and $\eta_p$ retain ~70% of the original value. Such an enhancement in device stability indicates the
additional advantages of the ZnO compared to low-work-function metals such as Ca and Mg, and insulating compounds such as LiF. The stability enhancement is mainly attributed to the hindrance of the penetration of moisture and oxygen from cathode side, which reduces the possibility of insulating CdSe surface, etching the PEDOT:PSS – active layer interface, and generating an insulating Al₂O₃ layer at the active layer – Al interface. In addition, the physical isolation of the active layer from Al cathode also prevents the potential chemical reaction of Al with the conjugated polymers and retards the degradation of the polymer – Al interface.¹⁷³

5.6 Summary

This chapter describes the introduction of a solution-processed ZnO nanoparticle layer to hybrid photovoltaic cells, resulting in both significantly enhanced efficiency and environmental stability. Hybrid solar cells based on P3HT and CdSe nanoparticles with a ZnO NP layer show ~50-90% increase in ηₚ, which is primarily contributed from an
increase in $J_{sc}$ and secondly from FF. Though only spherical CdSe nanocrystals and P3HT were tested in this study, the concept of inserting a solution-processed ZnO NP cathode interlayer to enhance device performance is applicable to the devices using anisotropic CdSe nanocrystals, other conjugated polymers and beyond.

The roles of the ZnO NP layer in hybrid solar cells have been systematically studied. The ZnO NP layer mainly serves to smoothen the hybrid active layer to provide better contact with Al cathode, adjust the optical field distribution inside the active layer for more optimal absorption, prevent the hole leakage from the active layer to the cathode, assist in extraction of photogenerated electrons, and prevent the direct quenching of photogenerated exciton at the active layer – Al interface. Furthermore, the ZnO NP layer also prevents the penetration of moisture and oxygen and the leakage of Al atom or cluster into the active layer, which together leads to a dramatic improvement in device environmental stability with ~70% efficiency retained after exposure to the air for over 2 months.
6.1 Introduction

Modern synthetic chemistry enables chemists to tailor organic small molecules and polymers with desired chemical structures and physical properties, which broadens the application of organic materials to the fields originally occupied by inorganic materials. Drastic progress in organic solar cells during the past several years is a very example of technological improvement driven by the development of synthetic chemistry. Most of the newly-developed polymers primarily for organic solar cells can be also applicable in organic-inorganic hybrid photovoltaic cells, provided that the energy levels of the polymers are matched with those of inorganic nanocrystals. In fact, to date, organic materials for hybrid solar cells are mostly directly borrowed from organic solar cells, rather than specially tailored for interfacing with inorganic nanocrystals.\(^\text{18}\)

Although there is only \(\sim 30\text{vol.}\%\) of conjugated polymer in the active layer of an organic-inorganic hybrid solar cell, the polymer contributes \(> 80\%\) photocurrent generation due to the high absorption coefficient \((\sim 10^5 \text{ cm}^{-1})\). Moreover, the open-circuit voltage of organic-based PV cells is generally proportional to the energy offset of acceptor LUMO level and donor HOMO level.\(^\text{174}\) Thus, the design rules for organic donor materials in term of electronic structure are as follows: a low energy gap to harvest most of the solar photons, and an appropriate energy level alignment with nanocrystal acceptor to facilitate efficient charge transfer and simultaneously create the highest energy offset with acceptor LUMO level.\(^\text{174}\) One common strategy to synthesize low-gap polymers is co-polymerizing an electron-rich unit with an electron-deficient unit,
such as PCPDTBT\textsuperscript{125} with energy gap of 1.45 eV as shown in Figure 6-1 and Figure 6-2. Due to the inter-chain charge transfer, the high LUMO level of the electron-rich unit (acceptor) and the low HOMO level of the electron-deficient unit (donor) define the ultimate energy gap. Introducing a strong electron-withdrawing unit or group like fluorine atoms into backbone of conjugated polymers is a means to reduce both the HOMO and LUMO levels with energy gap retained such as PB\textsubscript{n}DT-FTAZ.\textsuperscript{175} As shown in Figure 6-1 and Figure 6-2, compared to P3HT, PB\textsubscript{n}DT-FTAZ has almost the same energy gap but lower HOMO level (5.36 eV).

Bulk heterojunction photovoltaic cells critically rely on the uniform and nanometer-scale-accurate phase separation of donor and acceptor materials for efficient exciton diffusion and charge carrier collection.\textsuperscript{16, 135} Organic-inorganic hybrid
Figure 6-2. (color) UV-Vis absorption spectra of conjugated polymers and CdSe nanocrystals in dissociated states.

Materials have an organic phase (organic small molecule or conjugated polymer) and an organic-inorganic hybrid phase (colloidal nanocrystals having an inorganic core and a monolayer of organic surfactant). The miscibility of the organic component and the colloidal nanocrystal component in a particular system is a great challenge for their vast difference in affinity with organic solvents. Moreover, the processing conditions for colloidal nanocrystals are relatively similar, while those of conjugated polymers could be a huge difference. In addition, the molecular packing\textsuperscript{122} of the organic component and the phase separation\textsuperscript{176} of the organic–inorganic hybrid materials are also dependent on the post-processing treatment, such as solvent or thermal annealing.

In this chapter, we endeavor to enhance photocurrent and photovoltage of organic-inorganic hybrid photovoltaic cells through selecting conjugated polymers with different energy gaps and energy levels. Besides, we exemplify the effect of conjugated
polymers on processing conditions in organic-inorganic hybrid morphology and their corresponding device performance. In addition, as suggested in Chapter 5, the effect of a ZnO NP layer on hybrid PV cells will be further strengthened using the low-gap polymer PCPDTBT.

**6.2 PCPDTBT:CdSe Hybrid Processing on Device Performance**

**6.2.1 Phase Separation of PCPDTBT:CdSe Hybrid Thin Films**

Phase separation of donor and acceptor materials is of significant importance for bulk heterojunction hybrid solar cells.\textsuperscript{107, 135} PCPDTBT:CdSe hybrid thin films were prepared using chlorinated solvent/pyridine co-solvents (v/v 90/10) with concentration of

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Figure 6-3. (color) Tapping mode AFM topological (a, c, e) and phase (b, d, f) images of PCPDTBT:CdSe NP hybrids processed from different chlorinated solvent:pyridine mixtures. The volume ratio of chlorinated solvent/pyridine is 90/10.
3 mg PCPDTBT and 30 mg CdSe nanoparticles. The AFM topological and phase images of these films are shown in Figure 6-3. Though all films show sub-100 nm size domains that consist of both PCPDTBT and CdSe nanoparticles as evidenced from phase images, the film roughness and uniformity of the domain are very different. The film processed from chloroform (CF) : pyridine co-solvent shows a relatively wide domain size distribution (30 – 90 nm), and a high surface roughness (root-mean-square, R_{rms}, 9.2 nm) due to domain clustering. The film processed from chlorobenzene (CB) : pyridine co-solvent shows smaller and more uniform domain of 30 – 50 nm and much smoother surface with an R_{rms} of 2.7 nm. The domain size has been increased to 60 – 100 nm when processed from o-dichlorobenzene (DCB) : pyridine co-solvent that is larger than those processed from both CF and CB; but the R_{rms} is 6.9 nm, even smaller than the CF film.

The vast difference in hybrid film morphology is not only attributed to the hybrid-solvent affinity but also the physical properties of co-solvents themselves, particularly the solvent evaporation rate. CF has a boiling point of 62 °C and a high evaporation rate of 11.6 with reference of butyl acetate as 1, which leads to fast evaporation of chloroform during spin-coating and results in forming large domains; while pyridine has a boiling point of 115 °C, 53 °C higher than chloroform, which may result in formation of the small domains. Thus, the wide domain size distribution and high surface roughness of CF-processed film are mainly due to fast evaporation rate of chloroform and large boiling point gap between chloroform and pyridine. CB has a high boiling point of 131 °C with only 16 °C gap to pyridine and evaporation rate of 1.1, which could result in narrow domain size distribution and thermodynamically-controlled domain size growth. The
even evaporation of CB and pyridine also led to smooth surface. o-DCB has an even higher boiling point of 180 °C and lower evaporation rate of < 1 and possesses of 90% in volume in DCB co-solvents, which enables thermodynamically-controlled growth of domain and also results in narrow domain size distribution. The higher R_{rms} compared to that processed from CB co-solvent may be due to the larger boiling point gap between DCB and pyridine.

We further studied the phase separation of CB-processed PCPDTBT:CdSe hybrid films using TEM. The thickness of the hybrid films was varied in order to probe phase separation in a finer length scale. As shown in Figure 6-4a, hybrid film with 10-20 nm thickness shows uniform distribution of nanoparticles in the whole film and nanoparticles tend to connect each other. If the hybrid film thickness increased to ~30 nm, no nanoparticle aggregation has been observed yet a small degree of nanoparticle percolated network appeared. Further increasing the film thickness to ~ 50 nm and then ~ 80 nm (the device thickness) also does not lead to nanoparticle aggregation, but rather, the obvious formation of percolated network of nanoparticles. This nanoparticle phase has size 6-15 nm (1-2 times of individual nanoparticle size) and is uniformly distributed throughout the entire film. Such a high level of delicate phase separation together with large interfacial area between the polymer and nanocrystals ensure efficient exciton diffusion and subsequent carrier transport. In comparison, the early work by Huynh et al.\textsuperscript{16} showed a significant extent of nanoparticle aggregation and inhomogeneous distribution of nanoparticles for P3HT:CdSe hybrid film processed from CF, which leads to large phase separation of polymers (>50 nm), much higher than the exciton diffusion length. The difference in phase separation between this work and the
early publications may be attributed to the use of processing solvents. The evaporation rate of CF may be too fast to form uniform polymer and nanocrystal phases, while CB has much lower evaporation rate that ensures the formation of uniform and energetically-favored polymer and nanocrystal phases.

Figure 6-4. TEM images of PCPDTBT:CdSe NP hybrids with different film thickness processed from CB:pyridine mixtures. (a). 10-20 nm; (b). ~ 30 nm; (c). ~ 50 nm; (d). ~80 nm. The average size of CdSe NPs: 6.8 nm, and scale bars: 20 nm.

6.2.2 Effect of Processing Solvents on Device Performance

PCPDTBT:CdSe hybrid PV cells were fabricated using different processing solvents. The thicknesses of the active layer and the ZnO NP layer are ~80-100 nm and 25-30 nm as determined by ellipsometry, respectively; and the CdSe nanoparticles are 6.1± 0.3 nm. Figure 6-5a shows the J - V characteristics of the hybrid PV cells under 1 sun AM 1.5G simulated illumination. The photovoltaic performance parameters, and
Figure 6-5. (color) J - V characteristics (a) and EQE (b) of hybrid PCPDTBT:CdSe NP PV cells with the active layers processed from different chlorinated solvent/pyridine mixtures. Domain size and surface roughness of the active layers are summarized in Table 6-1. The CF device shows a $J_{sc} = 3.6$ mA/cm$^2$ and a $V_{oc} = 0.72$ V; while the $J_{sc}$ has been increased to $6.2$ mA/cm$^2$ using DCB as processing solvent yet $V_{oc}$ is relatively unchanged. The $J_{sc}$ has been further increased to $8.1$ mA/cm$^2$ when CB used as the solvent, accompanying with a slight increase in $V_{oc} = 0.78$ V.

The EQE spectra as a function of incident light wavelength were collected and shown in Figure 6-5b. All three devices show photovoltaic response from 350 nm to $>800$ nm, but the values and spectra of EQE are quite different. Both the CB and DCB
devices have much higher EQE than the CF device at 400 nm < λ < 600 nm that corresponds to the nanocrystal absorption, suggesting that a more uniform phase separation leads to better charge extraction through the nanocrystal network and polymer matrix. The corresponding enhancement in FF (from 36% of CF device to 46% of CB and DCB devices) also confirms the benefit of increased phase separation. The EQE for the CF and DCB devices at λ > 650 nm (corresponding to the PCPDTBT absorption) is considerably low, indicating the inefficient exciton dissociation resulting from too large domain size or insufficient phase separation. On the contrary, the CB-processed film has the most uniform and delicate phase separation that leads to the much higher EQE at λ > 550 nm, suggesting balanced morphology for efficient exciton dissociation and charge carrier extraction.

We also used mixed chlorinated solvents to process the PCPDTBT:CdSe hybrid films for device fabrication. As shown in Figure 6-6 and Table 6-1, $J_{sc}$ increases as the volume concentration of CB ($V_{CB}$) increases in both solvent systems. The $R_{rms}$ values and domain sizes of these films monotonically decrease as the $V_{CB}$ increases in both solvent systems. Furthermore, $\eta_p$ follows the similar trends as $J_{sc}$; and FF is relatively unchanged for CB:DCB system but has a sharp increase as the $V_{CB}$ increases from 0% to 20% for CF:CB system. Hence, as expected yet empirical, hybrid films with the smoothest surface and the smallest and most uniform domain lead to the highest photocurrent, FF, $V_{oc}$, and consequently the best $\eta_p$ in hybrid PV cells.

6.2.3 Effect of Annealing Temperature on Device Performance

Post-deposition thermal treatment is the other strategy to manipulate phase separation of donor and acceptor materials, which has been well demonstrated as a means to improve the performance of both organic and hybrid PV cells using P3HT as
donor material. However, the study by Heeger and co-workers showed that thermal annealing does not enhance the performance of polymer solar cells using the amorphous low-gap polymer PCPDTBT. Here we show that appropriate thermal annealing is still of great benefit for PCPDTBT:CdSe hybrid PV cells processed from CB system. As shown in Figure 6-7, though device without thermal annealing shows the lowest dark current, it also exhibits the lowest photocurrent and FF. The $J_{sc}$ increases 2-3 times as the annealing temperature increases; while a decrease in $J_{sc}$ has been observed once annealing temperature increased to 180 °C. The thermal annealing may lead to the further segregation of the nanocrystal and polymer components and thus
Table 6-1. Summary of performance parameter of PCPDTBT:CdSe hybrid solar cells processed by different solvent mixtures and related surface roughness and domain size of the active layer.

<table>
<thead>
<tr>
<th>Solvent mixture*</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$\eta_p$ (%)</th>
<th>$R_{rms}$ (nm)</th>
<th>Domain (nm)</th>
</tr>
</thead>
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<tr>
<td>CF</td>
<td>3.6</td>
<td>0.716</td>
<td>36.1</td>
<td>0.9</td>
<td>9.2</td>
<td>62 ± 21</td>
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<tr>
<td>CF:CB (80/20)</td>
<td>4.6</td>
<td>0.741</td>
<td>41.4</td>
<td>1.4</td>
<td>6.2</td>
<td>42 ± 13</td>
</tr>
<tr>
<td>CF:CB (50/50)</td>
<td>4.9</td>
<td>0.724</td>
<td>43.1</td>
<td>1.5</td>
<td>6.9</td>
<td>39 ± 11</td>
</tr>
<tr>
<td>CF:CB (20/80)</td>
<td>5.4</td>
<td>0.734</td>
<td>42.3</td>
<td>1.7</td>
<td>6.1</td>
<td>39 ± 11</td>
</tr>
<tr>
<td>CB</td>
<td>8.1</td>
<td>0.783</td>
<td>45.7</td>
<td>2.9</td>
<td>2.7</td>
<td>39 ± 8</td>
</tr>
<tr>
<td>CB:DCB (50/50)</td>
<td>7.7</td>
<td>0.731</td>
<td>44.5</td>
<td>2.5</td>
<td>4.7</td>
<td>46 ± 12</td>
</tr>
<tr>
<td>CB:DCB (20/80)</td>
<td>6.9</td>
<td>0.726</td>
<td>43.5</td>
<td>2.2</td>
<td>6.1</td>
<td>52 ± 13</td>
</tr>
<tr>
<td>DCB</td>
<td>6.2</td>
<td>0.724</td>
<td>45.7</td>
<td>2.1</td>
<td>6.9</td>
<td>74 ± 14</td>
</tr>
</tbody>
</table>

* Volume percent.

more defined nanocrystal and polymer phases. Furthermore, the remaining solvent residues such as pyridine that can weakly-bound nanocrystal surface can be removed upon annealing, leading to reducing the recombination centers for photogenerated excitons and charge carriers. Finally, the further removal of pyridine ligands together with the thermal activation may lead to more intimate connect between nanocrystals, resulting in better electron transport as indicated in the corresponding enhancement of FF.

6.3 Effect of the ZnO Layer on the PCPDTBT Device Performance

6.3.1 Device Efficiency

The study in chapter 5 unambiguously indicates both the efficiency and air-stability of hybrid PV cells can be enhanced by including a solution-processed ZnO NP layer between the active layer and the cathode. Here we extend to study this ZnO effect
in hybrid PV cells using conjugated polymers rather than the archetypical P3HT and also demonstrate the compatibility of low-gap polymers in hybrid PV cells for harvesting near-infrared photons. Figure 6-8 shows the $J-V$ characteristics of hybrid PV cells using 6.8 nm CdSe particles but different conjugated polymers under simulated 1 sun AM 1.5G illumination. The PCPDTBT device without a ZnO layer shows $J_{sc} = 7.2$ mA/cm$^2$ and $\eta_p = 2.7\%$, both of which are higher than the P3HT device with a ZnO layer, indicating the compatibility of the low-gap polymer in hybrid PV cells.$^{167}$ The PCPDTBT
device with a ZnO NP layer shows \( J_{sc} = 9.2 \, \text{mA/cm}^2 \), \( V_{oc} = 0.77 \, \text{V} \), \( \text{FF} = 0.49 \), and \( \eta_p = 3.5\% \), representing ~30\% enhancement compared to the device without a ZnO layer. Note that the efficiency of the device with a ZnO layer is comparable to those of the devices using CdSe nanorods and tetrapods and PCPDTBT.\(^{178}\)

Figure 6-8. (color) \( J - V \) characteristics of hybrid PV cells based on 6.8 nm CdSe particles and different conjugated polymers under 1 sun AM 1.5G illumination.

The PCPDTBT devices were also tested under variable illumination intensity \( (P_0) \), as shown in Figure 6-9. The \( V_{oc} \) of the devices without and with a ZnO layer closely follows a linear relationship with \( \ln P_0 \), as derived from the Shockley diode characteristics.\(^{19}\) The FF varies within 0.4 – 0.5 across the illumination range and the device with a ZnO layer has slightly higher FF, particularly at high \( P_0 \). The ratio of \( J_{sc} \) to \( P_0 \), corresponding to the external quantum efficiency, decreases ~30\% as the \( P_0 \) increases for both cells, suggesting the presence of strong bimolecular recombination\(^{179}\) and the addition of a ZnO NP layer does not alleviate this loss. The presence of the recombination and trapping sites in the nanocrystal surface / interface together with the
Figure 6-9. (color) Effect of a ZnO NP layer on the performance of hybrid PV cells using a low-gap polymer as donor material tested under variable illumination intensity.

relatively low mobilities of PCPDTBT and CdSe nanoparticles are the possible reason for such strong bimolecular recombination.\(^{61}\) Hence, the device without a ZnO layer leads to a highest \(\eta_p = 2.8\%\) at \(P_0 = 10\) mW/cm\(^2\); while the device with a ZnO layer yields a maximum \(\eta_p = 3.7\%\) at \(P_0 = 40\) mW/cm\(^2\), both are slightly higher than those at 1 sun condition.

The EQE has also been measured as a function of wavelength, as shown in Figure 6-10a. The device without a ZnO layer shows EQE of 45\% at 420 ≤ \(\lambda\) ≤ 450 nm and > 10\% at 600 nm ≤ \(\lambda\) ≤ 750 nm, indicating the photocurrent contribution from infrared photons. The device with a ZnO layer shows much higher EQE at \(\lambda \geq 500\) nm, which is of benefit for solar cells based on low gap polymers and with low electron mobility. The \(J_{sc}\) yielded by integrating the EQE spectra with the standard 1 sun AM 1.5G spectrum for the devices without and with a ZnO layer are 6.6 mA/cm\(^2\) and 8.7 mA/cm\(^2\), respectively, which are within the 5-10\% errors of the experimental results. The internal quantum efficiency, which is the ratio of the numbers of the collected electrons to the numbers of absorbed photons, has also been calculated by dividing the EQE by...
the total light absorption efficiency. The total light absorption efficiency of the active layer was corrected based on the published method.\textsuperscript{180} It is interesting to find the IQE of the device with a ZnO layer is higher than that of the device without a ZnO layer at almost entire photoresponsive range, suggesting the device with a ZnO layer is more efficient in charge transport / collection. The highest IQE for the device with a ZnO layer is \textasciitilde80\%, suggesting it is possible to achieve very high efficiency hybrid solar cells. Additionally, the high IQE also enables to enhance device efficiency by managing light absorption. In fact, the early demonstration using close-packed transparent polymer microlens arrays to enhance light harvesting witnessed 20-30\% increase in $\eta_p$.\textsuperscript{181}

![Figure 6-10](image)

Figure 6-10. (color) Effect of the ZnO NP layer on the external and internal quantum efficiencies of PCPDTBT:CdSe hybrid PV cells.

6.3.2 Role of the ZnO NP Layer

The roles of the ZnO NP layer in hybrid PV cells have already been discussed in chapter 5, which indicates the combination of electronic, optical, and morphological effects. Here we do not intend to over-emphasize these effects, but rather, illustrate the specific effects upon the low-gap polymer. Similarly, the ZnO NP layer smoothenes the PCPDTBT:CdSe layer from $R_{rms}$ of 5.9 nm to 3.0 nm, blocks the hole diffusion to the
cathode, and eliminates the direct contact at the hybrid – Al cathode interface to prevent exciton quenching. In particular, the ZnO layer can shift the higher optical intensity spectral range within the active layer to long wavelengths. The optical field profiles calculated based on transfer-matrix theory\textsuperscript{14} as shown in Figure 6-11 do show that the optical intensity of the PCPDTBT:CdSe hybrid active layer shifts to long wavelength when a ZnO layer included. This optical effect has been reflected in the EQE, which is much higher at $\lambda > 500$ nm for the device with a ZnO layer. In addition, this optical effect enables to tune the absorption of the active layer by varying the ZnO layer thickness and consequently the device photocurrent. This argument has been well demonstrated based on optical simulation with an assumption of unity IQE. Figure 6-11c shows the $J_{sc}$ of the device is as a function of both the thickness of the active layer and the thickness of the ZnO layer. The maximum $J_{sc}$ as predicted by optical simulation appears at positions where the thickness of an active layer is 70 – 100 nm and the thickness of a ZnO layer is ~20 nm, which is consistent with our experimental results.

### 6.3.3 Device Stability

The unencapsulated PCPDTBT:CdSe/ZnO device stability has also been tracked in a daily / weekly manner. As shown in Figure 6-12, the $J_{sc}$ falls more sharply at the initial testing days and then gradually reaches to a stable plateau. The $\eta_p$ follows the similar trend as $J_{sc}$, because both $V_{oc}$ and FF are relatively stable within the testing period. A closer observation reveals a slight increase in $V_{oc}$, which is attributed to the decrease in dark current during the tracking period. The slight decrease in FF is likely due to the decrease in charge carrier mobilities originated from the morphological change of the hybrid active layer or just the electron mobility decrease due to the insulating passivation of CdSe surface by moisture / oxygen. After > 2 months’ storage,
Figure 6-11. (color) Optical intensity profiles of the PCPDTBT:CdSe hybrid PV cells without (a) and with (b) a ZnO layer, and the calculated short-circuit current density of the PCPDTBT:CdSe hybrid PV cells as a function of active layer and ZnO layer thicknesses (c).

Both the $J_{sc}$ and $\eta_p$ retain ~70% of their original values, which is similar to that of the P3HT device. The environmental stability enhancement is again mainly due to the prevention of moisture / oxygen by the ZnO layer as discussed in chapter 5.

Figure 6-12. (color) Evolution of the photovoltaic performance parameters of an unencapsulated PCPDTBT:CdSe hybrid PV cell with a ZnO NP layer upon exposure to the ambient condition.
6.4 Enhancing Photovoltage Using a Deep-HOMO Polymer

The open-circuit voltage, another important factor determining the efficiency of a PV cell, is also tunable through tailoring the energy levels of conjugated polymers in organic-based solar cells. Here we demonstrated the $V_{oc}$ enhancement in hybrid PV cells by using a polymer with deep-HOMO.

As shown in Figure 6-1, a new copolymer $\text{PB}_n\text{DT}$ has a HOMO level of 5.36 eV, lower than 5.1 eV of P3HT and 5.2 eV of PCPDTBT. Its optical gap is 2.0 eV, only slightly higher than P3HT (1.9 eV) (Figure 6-2). Also, $\text{PB}_n\text{DT}$ shows the same order of magnitude in hole mobility as P3HT ($10^{-3} \text{ cm}^2\text{v}^{-1}\text{s}^{-1}$) as measured by SCLC in a BHJ structure. Hence, these properties suggest that $\text{PB}_n\text{DT}$ is a promising donor material for BHJ polymer-based solar cells with potential high $V_{oc}$ and efficiency.

Figure 6-13a shows the $J - V$ characteristic of hybrid PV cells based on CdSe nanoparticles ($\sim 6.8$ nm) and the medium gap polymer P3HT or $\text{PB}_n\text{DT}$. The $\text{PB}_n\text{DT}$ cell shows $J_{sc}$ as high as 7.9 mA/cm$^2$, $V_{oc} = 0.82$ V, FF = 0.50, and $\eta_p = 3.2\%$, indicating higher photocurrent and photovoltage than those of the P3HT cells. To the best of our knowledge, this is the first hybrid PV cell showing efficiency over 3% using a medium-gap polymer. The energy offset ($\Delta E$) for P3HT:CdSe system is $\sim 1.1-1.3$ eV (setting 7 nm CdSe CB as 3.8-4.0 eV), around 0.2-0.3 eV lower than that of the $\text{PB}_n\text{DT}$:CdSe system (1.3-1.6 V), suggesting there is more significant loss in photovoltage in the $\text{PB}_n\text{DT}$:CdSe system and further optimization is necessary to realize its full potential.

The $\text{PB}_n\text{DT}$:NRs cell show EQE $\sim 60\%$ at $490$ nm $\leq \lambda \leq 540$ nm, while the EQE of P3HT cell is $< 45\%$ at this region (Figure 6-13b). Besides, the $\text{PB}_n\text{DT}$ cell has higher EQE than the P3HT cell at $450$ nm $< \lambda < 600$ nm that mainly corresponds to the polymer absorption, suggesting that $\text{PB}_n\text{DT}$ is more efficient in hole transport in the BHJ
structure. This is also confirmed by the pioneer report, in which PBnDT:fullerene solar cells with active layer > 1 μm in thickness can still be very efficient.\(^{175}\)

Compared to the P3HT cell, the PBnDT cell shows 0.06 V increase in \(V_{oc}\), mainly due to the larger energy difference between nanocrystal LUMO and polymer HOMO. The \(V_{oc}\) of PBnDT-based hybrid PV cells can be as high as 0.89 V if CdSe nanorods were used as acceptor material (due to the raising in nanorod CB, Figure 6-14). Such a high \(V_{oc}\) together with rational \(J_{sc}\) make it very promising for polymer-based tandem solar cells.
Figure 6-14. (color) $J-V$ characteristic of a hybrid PV device based on CdSe nanorods and PBnDT. The nanorods have width 3.2 nm and AR10. The active layer was treated with ethanedithol before Al deposition (see Chapter 7). The PBnDT:CdSe NR device was processed from chlorobenzene :pyridine co-solvent.

6.5 Summary

In this chapter we demonstrate both the photocurrent and photovoltage of hybrid photovoltaic cells can be improved by customizing conjugated polymers and optimizing processing conditions. The processing of PCPDTBT:CdSe hybrid has been comprehensively studied, which indicates the processing solvent and annealing temperature have a profound impact upon the phase separation and ultimately the device performance. In particular, the surface roughness and domain size of nanoparticle-based hybrid films are drastically dependent on the processing solvent. Besides, appropriate thermal annealing has also been shown to be of benefit in enhancing device performance, probably due to more optimal phase segregation and further removal of exciton and charge carrier recombination/trap centers.
The photoresponsive wavelength of hybrid PV cells has been extended to ~850 nm using the low-gap polymer PCPDTBT. The concept of including a ZnO layer between the active layer and the cathode has been further proved in the hybrid PV cells based on PCPDTBT, which leads to $J_{sc} \sim 9$ mA/cm$^2$ and $\eta_p$ 3.5% under 1 sun AM 1.5G illumination. Similarly, the ZnO layer smoothens the active layer, serves as optical spacer, eliminates the direct contact between the hybrid and the cathode, assists in extraction of photogenerated electron, and prevents hole diffusion to the cathode. In addition, the tracking study in a 2-month period indicates the PCPDTBT cell with a ZnO layer is more resistive to the moisture and oxygen penetration, resulting in ~70% efficiency retained.

Moreover, we also demonstrate the improvement in the open-circuit voltage of hybrid PV cells using a conjugated polymer with deep HOMO (PB$_n$DT-FTAZ). The PB$_n$DT:CdSe NP cell shows $V_{oc} > 0.8$ V and $\eta_p \sim 3.2\%$, which, for the first time, the hybrid PV cells based on a medium-gap polymer and spherical CdSe nanoparticles show $\eta_p > 3\%$. The $V_{oc}$ reaches to as high as 0.89 V when CdSe nanorods are used as the acceptor materials in hybrid PV cells, suggesting the promising candidate in polymer-based multi-junction solar cells.
CHAPTER 7
ENGINEERING POLYMER-NANOCRYSTAL INTERFACE BY CHEMICAL TREATMENT

7.1 Introduction

Though significant efforts have been made to tailor both conjugated polymers and colloidal nanocrystals, the performance of organic-inorganic hybrid photovoltaic cells still lags behind their all-organic counterpart. The reason for this disparity lies in the fundamental difference between two materials systems. In particular, the complex surface of colloidal nanocrystals creates a polymer–nanocrystal interface that governs the electronic and morphological interactions and consequently affects the performance of organic-inorganic hybrid solar cells.\(^{182}\)

The primary concern to introduce inorganic nanocrystals into organic solar cells is to enhance the electron affinity and transport,\(^{33}\) which, to a large extent, has been compromised by the fact that the charge carrier mobility of colloidal nanocrystals is dropped by several orders of magnitude to a level of typical organic semiconductors.\(^{61}\) Again, such low mobility is attributed to the abundant surface and interface of nanocrystals involving organic surfactants. Other than that, the presence of these organic surfactants can also serve as recombination centers / traps for photogenerated excitons and charge carriers, which further deteriorates the photocurrent generation in a solar cell involving colloidal nanocrystals. Therefore, these challenges undermine the potential advantages of organic-inorganic hybrid photovoltaic cells.

In this chapter, we stress the importance of engineering the polymer-nanocrystal interface to bridge the performance gap between hybrid solar cells and all-organic counterparts. The different types of ligands present upon nanocrystal surfaces can be selectively removed by various chemical treatments. In particular, the removal of
negatively-charged X-type ligands significantly improves the charge transport properties as well as reduces the electronic trap density, which together lead to significant enhancement in the performance of hybrid solar cells.

**7.2 Synthesis and Processing of CdSe Nanorods**

CdSe nanorods were synthesized according to the published procedures.\(^{30}\) Briefly, 0.205 g of CdO (Alfa Aesar, 99%), 2.90 g of TOPO (Sigma-Aldrich, 99%), and 0.851 g of TDPA (PCI synthesis, 97%) were mixed and heated to 320 °C under N\(_2\) flow. The mixture was maintained at this temperature to get a clear solution, and then naturally cooled to room temperature. After 24 h aging, the mixture was re-heated to 320 °C under N\(_2\) flow. Selenium stock solution (62 mg Se, Sigma-Aldrich, 99%; 0.30 mL tributylphosphine (TBP), Sigma-Aldrich, 90%; 1.0 mL TOP, Sigma-Aldrich, 90%; and 0.30 mL toluene) was injected, and the reaction was kept for 40 min at 300-310 °C for nanorods with low AR ~2 and length 14 nm, and at 250-260 °C for nanorods with high AR ~7 and length 32 nm (Figure 7-1). The reaction was terminated by naturally cooling to room temperature within 10-15 min.

As-prepared CdSe nanorods were purified by dissolving in toluene and precipitation with methanol 6 times. After purification, nanorods were ligand-exchanged in pyridine. CdSe nanorods (~80 mg) were mixed with 15 mL pyridine, and then refluxed for 24 h under N\(_2\) flow. The nanorods were recovered by precipitation with hexane and centrifugation. Polymer:CdSe nanorod hybrids were prepared by dispersing 30 mg CdSe nanorods into 1 mL chloroform followed by mixing with 3.0 mg of P3HT or PCPDTBT.
7.3 CdSe Nanorods and Polymer:CdSe Hybrid Film Characterization

7.3.1 TEM Measurement

The size of the CdSe nanorods was characterized using a JEM-2010F transmission electron microscope (TEM) with a 200 keV electron beam energy. CdSe nanorods in toluene solution were dropped onto a carbon-coated copper grid and naturally dried before measurement.

The hybrid thin film samples were prepared as follows for TEM measurement. First, P3HT:CdSe hybrid film was spin-coated upon ITO substrates pre-coated with a layer of PEDOT:PSS. The active layer was treated by ethanedithiol (EDT) in acetonitrile with volume ratio of 1% if necessary and then annealed at 120 °C for 20 min. After that, the hybrid films were immersed into deionized water to dissolve the PEDOT:PSS layer and make the hybrid active layer floated upon the water surface. The floated active layer was picked up by the carbon-coated copper grid. The TEM measurement was performed in a JEOL 200CX with accelerating voltage of 200 KeV.

Figure 7-1. TEM images of CdSe nanorods with different aspect ratio.
7.3.2 FTIR Measurement

CdSe nanorods in chloroform solution with a concentration of 5 mg/mL were spin-coated on top of glass substrates, and then treated with EDT or without any more treatment. Then nanorod films were annealed at 120°C for 20 min and re-dissolved into chloroform and uniformly deposited onto a sodium chloride substrate. The FTIR spectra were collected using a Perkin FTIR spectrometer. For quantitative calculation, we chose the absorption spectrum of the –CH₃ group, since both the TOPO and PA molecules have methyl groups. Here we only consider TDPA for PA molecules and PPA excluded for relatively low concentration. Since only TOPO molecules can be removed during pyridine exchange and remaining PA molecules removed after EDT treatment and based on Lambert-Beer law \( A = \alpha \cdot b \cdot c \), where \( A \) is absorbance, \( \alpha \) is extinction coefficient, \( b \) is path length, and \( c \) is concentration, we can quantitatively determine the percentage of organic surfactants removed after each treatment. The concentration for purified sample and pyridine-exchanged sample is the same and twice of that of EDT-treated sample.

7.3.3 NMR Measurement

For \(^{31}\)P NMR measurement, saturated solutions of the CdSe nanorods in CDCl₃ were used in all NMR recordings. For the sample exchanged by pyridine, we collected the ligands by removing the precipitated CdSe nanorods and evaporating the solvents. The collected white solids were re-dissolved in CDCl₃ for NMR study. For the ligands exchanged by the EDT, pyridine-exchanged nanorods in chloroform were added by a small amount of triethylamine and EDT, resulting in the precipitation of CdSe nanorods and concomitantly the removal of ligands present upon nanorod surface. The
chloroform solution was evaporated and organic ligands were collected and re-dissolved in CdCl$_3$ for NMR study.

Each recorded spectrum is a result of 2048 scans. The NMR experiments were done for solutions with and without added phosphoric acid standard vessel, so that the chemical shifts for $^{31}$P are referenced to the phosphoric acid standard ($^{31}$P at 0 ppm). $^{31}$P NMR spectra were recorded on a Varian VXR 300 spectrometer (300 MHz).

### 7.3.4 XPS Measurement

XPS data were collected using a PHI 6100 X-ray Photoelectron Spectrometer using a magnesium anode, a step size of 0.1 eV and a pass energy 17.9 eV. The signal-to-noise ratio was improved by accumulating data over 90 scans. The samples were prepared by spin-coating CdSe nanorods (30 mg/mL in chloroform) upon Si substrates. For the samples with thermal treatment, no more EDT treatment was performed. The XPS peaks were corrected for sample charging by referencing the main carbon peak to 284.6 eV, and the experimental data were fitted with Gaussian-Lorentian profiles. The binding energy of XPS peak has been corrected by referencing C 1s to 284.6 eV.

### 7.3.5 AFM Measurement

AFM measurement was performed on the devices with a Veeco Innova scanning probe microscope operating in tapping mode. The hybrid films were deposited upon ITO substrates pre-coated with a layer of PEDOT:PSS. The active layer was treated by EDT if necessary and then annealed at 120 °C for 20 min before measurement.

### 7.4 Effect of EDT Treatment on Device Performance

One-dimensional nanorods have been regarded as an advantage to provide direct charge transport pathways in electronic devices, which has already been
demonstrated in hybrid PV cells by several groups\textsuperscript{16, 170, 182} and in Chapter 4 as well. Thus, we synthesized CdSe nanorods using the high temperature injection method, alkylphosphonic acids and TOPO as main capping ligands, and TOPO as solvent. The volume, length, aspect ratio (AR) of CdSe nanorods can be tailored by controlling the reaction parameters. Here CdSe nanorods with two different aspect ratios were used for fabricating hybrid PV cells (Figure 7-1).

The polymer:CdSe hybrid PV cells have a structure of ITO/ PEDOT:PSS/ polymer:CdSe/ Al. The hybrid active layer was deposited by spin-coating the chloroform solution composed of pyridine-exchanged CdSe nanorods and conjugated polymers (P3TH or PCPDTBT) and have a thickness ~ 80-100 nm, and then was treated by acetonitrile solution containing 1\% EDT for 1 min. The devices were annealed at 120 °C for 20 min at a N\textsubscript{2}-filled glove box before Al deposition. All the devices were tested in the air under simulated AM 1.5 G solar illumination.

A phenomenon of time-dependent performance was observed for all the devices, which had also been observed in our previous study on P3HT:CdSe hybrid PV devices based on either spherical nanoparticles\textsuperscript{61} or anisotropic nanorods (Chapter 4). The device performance would reach a plateau after a few hours’ exposure to air and be stable at the plateau for several hours (Figure 7-2), where all the measurements have been conducted. Similarly, this aging effect has been attributed to the adsorption of water and oxygen molecules to CdSe nanorods surface through diffusion, which leads to the surface passivation and oxidation.

The effect of EDT treatment in enhancing the hybrid PV device performance is primarily evident in the $J - V$ characteristics under simulated 1 sun illumination, as
Figure 7-2. (color) Air exposure time dependent $J - V$ characteristics of PCPDTBT:CdSe NR hybrid PV cells under dark and 1 sun AM 1.5G illumination.

shown in Figure 7-3a and the corresponding PV parameters listed in Table 7-1. The device based on P3HT and CdSe nanorods with AR ~7 shows a significant increase in $J_{sc}$ from 5.9 mA/cm$^2$ to 7.4 mA/cm$^2$ after the EDT treatment. Together with a slight enhancement in both $V_{oc}$ and FF, the $\eta_p$ has been increased from 2.2% to 2.9% (Table 7-1).

The efficiency of hybrid PV device can be further enhanced by using low-gap polymers to harvest abundant infrared photons. As shown in Figure 7-3b and Table 7-1, a hybrid PV cell based on a low-gap polymer PCPDTBT and CdSe nanorods shows a $\eta_p = 3.3\%$ under 1 sun illumination. When the active layer treated with EDT, a substantial increase in $J_{sc}$ from 9.3 mA/cm$^2$ to 12.8 mA/cm$^2$ and a slight enhancement in
both $V_{oc}$ and $FF$ have been observed, leading to $\eta_p = 4.8\%$ under 1 sun illumination and after spectral mismatch correction. To the best of our knowledge, this is a record efficiency for bulk heterojunction hybrid PV cells based on conjugated polymers and colloidal nanocrystals.

The hybrid PV devices were further characterized under variable illumination intensities ($P_0$). As shown in Figure 7-3 for both P3HT:CdSe and PCPDTBT:CdSe devices, the ratio of $J_{sc}$ to $P_0$, corresponding to the external quantum efficiency, decreases as $P_0$ increases from 0.07 sun to 1.3 sun for the devices both without and with EDT treatment. This behavior suggests the presence of strong bimolecular recombination within the active layer and leads to the loss in photogenerated charge carriers. In particular, at high $P_0$, this loss becomes more serious due to the high carrier concentration and low charge carrier mobility in the active layer. Manipulating this loss is a must and still a challenge for bulk heterojunction organic-based solar cells.

The EDT treatment leads to ~10% and ~35% increase in $J_{sc}/P_0$ for the P3HT and PCPDTBT devices, respectively, suggesting partial suppression of the bimolecular recombination. Partly offset by the increase in $V_{oc}$ of $P_0$, a maximum $\eta_p$ of 2.6% and 3.2% both appeared at 0.07 sun, have been observed for P3HT:CdSe devices without and with EDT treatment, respectively. The maximum $\eta_p$ of 3.7% (at $P_0 = 0.07$ sun, without EDT treatment) and 5.2% (at $P_0 = 0.12$ sun, with EDT treatment) have been observed for the PCPDTBT devices, which is comparable to the all-organic PV cells based on the same donor PCPDTBT and PC71BM with additives during active layer processing.
Figure 7-3. (color) Performance enhancement in polymer:nanocrystals hybrid photovoltaic cells upon the EDT treatment. $J – V$ characteristics and Illumination power dependence of $\eta_p$, ratio of short-circuit current density ($J_{sc}$) to $P_0$, $V_{oc}$, and FF for P3HT:CdSe (a) and PCPDTBT:CdSe (b) hybrid PV devices with and without EDT treatment.

The external quantum efficiency spectra have been recorded to further evaluate the device performance upon EDT treatment (Figure 7-4). P3HT:CdSe device shows higher EQE at wavelengths from $350 \text{ nm} < \lambda < 600 \text{ nm}$ with EDT treatment and a maximum EQE of 56% was achieved at $\lambda = 375 \text{ nm}$. Meanwhile, the device based on PCPDTBT shows a broader photoresponse range at $300 \text{ nm} < \lambda < 850 \text{ nm}$ due to its lower optical gap (1.45 eV). The EDT treatment leads to higher EQE in the entire photoresponsive spectral range for the PCPDTBT:CdSe device, particularly at $\lambda < 750 \text{ nm}$, suggesting better balanced charge transport in the active layer. In particular, the fact that the EDT-treated devices show higher EQE at the short wavelength ($\lambda < 500 \text{ nm}$).
Table 7-1. Summary of photovoltaic performance under 1 sun AM 1.5 G illumination for polymer:colloidal nanocrystal hybrid photovoltaic cells.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CdSe NRs</th>
<th>EDT</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$\eta_p$ (%)</th>
<th>$\Delta \eta_p/\eta_p$ (%)</th>
</tr>
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<tbody>
<tr>
<td>P3HT</td>
<td>Low AR$^{(a)}$</td>
<td>no</td>
<td>4.9</td>
<td>0.73</td>
<td>0.39</td>
<td>1.4±0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>yes</td>
<td>7.1</td>
<td>0.71</td>
<td>0.51</td>
<td>2.6±0.2</td>
<td>86</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>Low AR$^{(a)}$</td>
<td>no</td>
<td>6.6</td>
<td>0.72</td>
<td>0.39</td>
<td>1.9±0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>yes</td>
<td>9.9</td>
<td>0.72</td>
<td>0.46</td>
<td>3.3±0.2</td>
<td>74</td>
</tr>
<tr>
<td>P3HT</td>
<td>High AR$^{(b)}$</td>
<td>no</td>
<td>5.9</td>
<td>0.72</td>
<td>0.52</td>
<td>2.2±0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>yes</td>
<td>7.4</td>
<td>0.73</td>
<td>0.54</td>
<td>2.9±0.2</td>
<td>32</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>High AR$^{(b)}$</td>
<td>no</td>
<td>9.3</td>
<td>0.72</td>
<td>0.49</td>
<td>3.3±0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>yes</td>
<td>12.8</td>
<td>0.74</td>
<td>0.50</td>
<td>4.7±0.3</td>
<td>42</td>
</tr>
</tbody>
</table>

$^{(a)}$ Low AR = 2 (length: 14 nm, width: 6.4 nm); $^{(b)}$ High AR = 7 (length: 32 nm, width: 4.4 nm).

nm) region indicates electron transport has been significantly improved, since the high-energy photons are more prone to be absorbed close to the anode side in a normal structure cell.\(^{177}\)

The performance of hybrid PV devices is also dependent on CdSe nanorods'
length and AR,\textsuperscript{16} partly because nanorods form the matrix for charge transport and their surfaces act as exciton dissociation and charge transfer sites. When nanorods with length 14 nm and AR \approx 2 used as acceptor, as shown in Figure 7-5 and Table 7-1, P3HT:CdSe hybrid PV device shows $\eta_p = 1.4\%$, \approx 50\% lower than those devices based on nanorods with AR \approx 7. However, when the active layer treated with EDT, the device exhibits a substantial improvement in $J_{sc}$ from 4.9 mA/cm$^2$ to 7.1 mA/cm$^2$ and also in FF from 0.39 to 0.51, which leads to \approx 85\% enhancement in $\eta_p$, significantly higher than 32\% enhancement for those devices with high-AR nanorods. Similarly, when low-AR nanorods blended with PCPDTBT, the device without EDT treatment shows $\eta_p = 1.9\%$ together with low $J_{sc}$ and FF; however, the device with EDT treatment witnesses a sharp increase in $J_{sc}$ and FF, thus resulting in 73\% improvement in $\eta_p$. The relative low performance for low-AR nanorod devices is likely due to the poor charge transport and much richer surface chemistry that may result in more exciton and charge carrier recombination sites. The more significant enhancement in device performance with EDT treatment also suggests the effect of the nanorod surface properties.

![Figure 7-5](image.png)

Figure 7-5. (color) $J - V$ characteristics (a) and EQE (b) of P3HT:CdSe NR PV devices based on shorter nanorods (AR: \approx 2).
The effect of chemical treatment on device performance has been further investigated by using different additives. Here we select two other additives to perform the same chemical treatment as EDT during device fabrication. One additive is 1, 8-octanedithiol (ODT) that has a similar chemical structure as EDT but with longer alkyl chain; the other one is 1,8-diiodooctane (DIO) that has the same alkyl chain length as ODT but has anchoring group iodine. The $J – V$ characteristics of hybrid PV cells based on CdSe nanorods with AR ~5 and under various chemical treatment were shown in Figure 7-6a. The device with the EDT treatment shows increased $J_{sc}$ and FF under 1 sun illumination compared to the device without treatment, resulting in a relative 20% enhancement in $\eta_p$. The device with the ODT treatment shows a significant decrease in $J_{sc}$ and FF compared to the untreated device. Though there is a slight increase in $V_{oc}$, the $\eta_p$ has been reduced by 25%, suggesting poorer charge transport with long-chain additive. The device performance has been further decreased when DIO used as treating agent, with less than 50% retained in $\eta_p$. It is very likely that DIO just exists as foreign additive within the active layer or weakly bound to the nanorod surface, and it is not likely that the as-bound ligands could be exchanged by DIO due to its relatively weak affinity. Thus, rather than acting to passivate nanorod surface, DIO may act as recombination centers and/or insulating sites to hinder charge transport.

The EQE of the hybrid PV cells using different additives has also been recorded as shown in Figure 7b. Similar to the device based on nanorods with AR ~7, the device with EDT treatment shows an enhancement in EQE at the entire wavelength range compared to the untreated device. However, the ODT and DIO devices show significant decrease in EQE in the entire wavelength range, which is consistent with the decrease
Figure 7-6. (color) $J – V$ characteristics (a) and EQE (b) of P3HT:CdSe NR PV devices with various chemical treatment. 

in photocurrent reflected in the $J – V$ characteristics. The uniform increase and decrease in EQE with chemical treatment further emphasizes the importance of the polymer-nanocrystal interface, which is the junction for exciton dissociation and the path for charge carrier transport.

7.5 Effect of EDT Treatment on Nanorods and Hybrid Films

7.5.1 UV-Vis Absorption

To understand the nature of the EDT treatment on the hybrid materials and the effect on the device performance, a series of optical, electrical, chemical, and structural characterization on hybrid materials have been carried out. Figure 7-7 shows the UV-Vis absorption spectra of P3HT:CdSe and PCPDTBT:CdSe hybrid films. The absorption of P3HT:CdSe and PCPDTBT:CdSe hybrid films is the superposition of the absorption of the individual polymer and CdSe. When treated by EDT, these films do not show apparent change in absorption, which suggests the EDT treatment does not result in changes in the bulk properties of the active layer, such as material gain / loss or
structural ordering. Again, any potential changes are likely concerned with the interfaces between the materials.

Figure 7-7. (color) UV-Vis absorption spectra of polymer:CdSe hybrid films.

7.5.2 Hybrid Film Morphology

The morphologies of the PCPDTBT:CdSe hybrid films without and with EDT treatment were also probed by tapping-mode AFM. As shown in Figure 7-8, large domains with size ~ 200 – 600 nm are observed for the film without the EDT treatment (Figure 7-8a). These domains do not correspond to either pure polymer or nanocrystal domains as suggested by the uniform phase image (Figure 7-8b). The close-up images shown in the inset reveal that each large domain consists of many smaller domains with size of ~ 30 – 50 nm, and these small domains are composed of both PCPDTBT and CdSe nanorods. The hybrid layer shows no noticeable change in the surface topology and the root-mean-square surface roughness remains at $R_{\text{rms}} = 10$ nm after the EDT treatment (Figure 7-8c), which is different to the appearance of extra pin-holes and micro-cracks in PbS quantum dot thin film after treatment by small molecules$^{184,185}$ and also different to polymer solar cells processed with additives that leads to drastic
Figure 7-8. (color) Surface morphology of PCPDTBT:CdSe hybrid films. Tapping mode atomic force microscopy (AFM) topographies and their corresponding phase images of PCPDTBT:CdSe NR hybrid films without EDT treatment (a, b) and with EDT treatment (c, d) (scale bar: 1 μm). Inset: close-up topographical image and the corresponding phase images (scale bar: 200 nm).

change in phase-separation\textsuperscript{135, 186}. However, the phase image (Figure 7-8d) does show an enhanced contrast for some regions among the small domains, suggesting a more rigid surface after the EDT treatment that may be due to the further removal of organic ligands from CdSe surface (details in section 7.6).

To further investigate the possible morphological change, we employed TEM to image P3HT:CdSe hybrid films. As shown in Figure 7-9 a-c, there are a number of white and black areas spreading across the entire image. The enlarged image indicates that these white and black areas are the P3HT:CdSe hybrid but have different nanorod loading concentrations with dark region having higher nanorod loading (Figure 7-9 b-c). CdSe nanorods are uniformly spreading over the hybrid film and not nanorod
aggregation has been observed. When EDT treated, as shown in Figure 7-9 d-f, there is no significant difference in morphology compared to the untreated samples. Neither higher degree of nanorod segregation nor phase separation has been observed for the treated samples. In addition, the open structure of hybrid film as clearly indicated in the magnified images has the advantage of EDT penetration into the inside for more efficient removal of the capping ligands (Figure 7-9 c, & e).

7.5.3 Chemical Treatment on Surface Chemistry of CdSe Nanocrystals

The EDT treatment does have a profound impact on the surface chemistry of CdSe nanorods as verified by FTIR, NMR, and XPS characterization. Organic surfactants TOPO and tetradecylphosphonic acid (TDPA) were involved during synthesis, which may bond to the nanocrystal surface to affect nanocrystal growth during synthesis and to stabilize nanocrystals after synthesis.²⁷, ²⁸ Figure 7-10a shows
the FTIR transmittance spectra of CdSe nanorods purified after synthesis, ligand-
 exchanged in pyridine, and treated by EDT. The absorption peaks at 2921 cm\(^{-1}\) and 
2847 cm\(^{-1}\) are due to the C-H stretching vibration in \(-\text{CH}_3\) groups from either TOPO or 
TDPA.\(^{187}\) The intensities of these absorption peaks are decreased after ligand-
exchange in pyridine and nearly vanish after EDT treatment, suggesting the alkyl chain 
ligands can be partly removed both by ligand-exchange with pyridine and by EDT 
treatment. Also, the presence of the absorption peaks at 1098 cm\(^{-1}\) and 931 cm\(^{-1}\) that 
correspond to the stretching vibration of P=O and P-O, respectively, suggests the 
abundance of TOPO and TDPA on the nanocrystal surface. These phosphor-containing 
ligands are only partially removed after ligand-exchange with pyridine, while they are 
more effectively removed by the EDT treatment.

The cleavage processes of organic ligands upon CdSe surface have been further 
investigated by phosphor nuclear magnetic resonance (\(^{31}\)P NMR). The purified CdSe 
nanorods dispersed in deuterochloroform (CDCl\(_3\)) with concentration \(~50\) mg/mL does 
not show any distinctive signal in \(^{31}\)P NMR. This behavior may be explained by the fact 
that the nanorod concentration (or the phosphor-containing ligands’ concentration) is 
is insufficient or the signal of the bounded ligands may be broadened due to the slow 
rotational correlation time of the nanorods. However, as shown in Figure 7-11, after 
ligand-exchange with pyridine, the exchanged ligands collected after precipitating 
nanorods do show a very sharp peak at 50.8 ppm, which can be assigned to the free 
TOPO.\(^{56}\),\(^{188-191}\) The appearance of TOPO also suggests it cannot be fully removed by 
common purification with toluene dissolution and methanol precipitation. Pyridine-
exchanged nanorods in CDCl\(_3\) have been further treated by the EDT with a small
amount of triethylamine (TEA) as a Lewis base (acetonitrile is not very miscible in CDCl₃). The nanorods were aggregated and precipitated after this treatment that was isolated by centrifugation, and the CDCl₃ solution was used for NMR characterization. The EDT-exchanged ligands exhibit three sharp peaks located at 26.7 ppm, 21.5 ppm and 18.7 ppm (Figure 7-11). The peaks at 26.7 ppm and 18.7 ppm can be assigned to the phosphors in TDPA and in P, P’-(di-n-tetradecyl) dihydrogen pyrophosphonic acid (PPA, created by the condensation of two TDPA molecules at high temperature or as impurity in source materials), respectively. The peak at 21.5 ppm may be due to the formation of either TDPA-TEA salt or PPA-TEA salt or an unknown alkyl phosphonic

Figure 7-10. (color) FTIR spectra of CdSe nanorods upon various treatments. (a). Full spectra, (b) absorption spectra of −CH₃ group.
acid species originating from the source materials.\textsuperscript{56,188-191} Thus, the NMR study indicates that pyridine-exchange can effectively remove the neutral "L-type" ligands like TOPO that typically bonds to the nanocrystals through weak van der Waals interaction; and the EDT treatment further remove the charged "X-type" ligands like TDPA and PPA that usually bonds to the nanocrystal surface through ionic or covalent interaction.

Figure 7-11. (color) \textsuperscript{31}P NMR spectra of ligands exchanged by pyridine (black curve) and ligands exchanged by EDT (red curve) from nanorods.

The selective removal of surface ligands by chemical treatment enables us to quantitatively estimate the population of each type of ligands. Here by integrating the absorption peaks of methyl group at 2921 cm\textsuperscript{-1} and 2847 cm\textsuperscript{-1} in FTIR spectra and based on Lambert-Beer law,\textsuperscript{187} 65±10% of organic ligands (primarily TOPO) are removed after ligand-exchange with pyridine and 90±10% of total ligands can be cleaved after further EDT treatment.

Though FTIR and NMR characterizations give a clear picture that surface ligands on the nanocrystals can be removed step-by-step by pyridine-exchange and then by EDT treatment, the detailed cleavage processes and the chemical bonding nature are still unclear. Here XPS was employed to probe the chemical states of various elements.
Figure 7-12a shows the C 1s XPS spectra for nanorods processed using various conditions. The intensity of the C 1s peak is reduced approximately by one-half after ligand exchange in pyridine. Additional EDT treatment without thermal annealing results in a slight increase in the C 1s intensity, which could be attributed to the absorption of EDT molecule to the CdSe surface. Further thermal annealing of the EDT-treated sample leads to a sharp reduction in the C 1s peak intensity, suggesting the removal of most organic ligands from the nanocrystal surface. The P 2p spectra appear to indicate a chemical shift of 0.5 to 0.8 eV between the purified, pyridine-exchanged, and EDT treated nanocrystal samples (Figure 7-12b); though the broad spectral distribution makes the result somewhat difficult to define. It is very likely that the chemical environments of these ligands have been changed after chemical treatment, as the peak of fitted curve shifts to higher binding energy that may correspond to the free alkylphosphonic acid species (Figure 7-12b, blue curve). However, it is more conclusive for the EDT treated sample after thermal annealing, where the XPS spectrum clearly shows the disappearance of P in the nanorod film, suggesting the removal of phosphor-containing ligands and being consistent with the FTIR result. Thus, the XPS results suggest that the EDT treatment process first results in the release of the alkylphosphonic acids from the nanocrystal surface, which are then removed from the films following thermal annealing.

Other than removing X-type ligands from nanocrystal surface with the EDT treatment, surface passivation is also envisioned for the strong affinity of mercapto group to the nanocrystals. It is challenging to investigate using XPS due to overlapping of the binding energies of S 2s and 2p states with those of Se 3s and 3p states,
respectively. As shown in Figure 7-12 c & d, the Se peaks at 160.0 eV (Se 3p\(_{3/2}\)), 165.5 eV (Se 3p\(_{1/2}\)), and 229.0 eV (Se 3s), which match well with the published XPS data for CdSe\(^{192}\) can be clearly identified. However, we can also identify peaks at 162.1 eV, 163.8 eV, and 227.1 eV, which correspond to S 2p\(_{3/2}\), 2p\(_{1/2}\), and 2s states, respectively. Moreover, the binding energies of the S 2s and S 2p\(_{3/2}\) states are 0.5 to 1 eV higher than the reported values for CdS but are ~1 eV lower than those for organic thiols. These peaks are matched with those of metal-thiolate.\(^{193}\) The surface S to Se ratio is estimated to be 30±10% based on the individual peak intensities. Thus, the EDT treatment results in the passivation of CdSe surface with a chemical state of Cd-thiolate, rather than either CdS or EDT molecule.

Figure 7-12. (color) XPS high-resolution spectra of CdSe nanorods upon various treatment. (a). C 1s, (b). P 2p, (c). Se 3p and S 2p, and (d) Se 3s and S 2s.
7.5.4 Charge Transport of Hybrid Films

The chemical characterization gives a clear picture of the removal of surface ligands, which could result in the change in charge transport properties of hybrid films. Here we fabricated electron-only and hole-only devices to determine the charge transport behaviors of PCPDTBT:CdSe hybrid films without and with the EDT treatment. The electron-only device has a structure of Al/ active layer/ Al and the hole-only device has a structure of ITO/ active layer/ Au. The $J-V$ characteristics of these devices are shown in Figure 7-13. According to Child’s law (eq.3-7) and inserting the parameters the same as used in Chapter 4, it is shown that the electron mobility has been increased from $\mu_e = 3 \times 10^{-6}$ cm$^2$/V·s to $6 \times 10^{-5}$ cm$^2$/V·s after the EDT treatment. The hole mobility remains at $\mu_h = 1 \times 10^{-5}$ cm$^2$/V·s after the EDT treatment, suggesting the EDT treatment mostly has an impact upon the nanocrystals.

7.6 Nature of the EDT Treatment on Device Performance

The various chemical characterizations clearly identify the existence of charged X-type ligands bounded to the CdSe surface. These X-type ligands have been regarded to form surface defect states that could quench excitons and trap charge carriers, which in turn result in the loss of photocurrent and photovoltage in a hybrid PV cell. Removal of these ligands from the nanocrystal surface and simultaneous passivation by formation of Cd-thiolate upon the EDT treatment lead to the removal of these surface defect states, which is certainly of benefit in reducing the exciton and charge recombination loss at the polymer – nanocrystal interface. This benefit has been well reflected in the huge enhancement in $J_{sc}$ and also slight increase in $V_{oc}$ of the hybrid PV cells with EDT treatment. Furthermore, the increase in electron mobility of hybrid film with the EDT treatment also confirms the reduction in charge recombination, which
Figure 7-13. (color) \( J \)-\( V \) characteristics of electron-only devices with a structure of Al/PCPDTBT:CdSe/Al using CdSe nanorods (AR: \( \sim 7 \)) (a) and hole-only devices with a structure of ITO/PCPDTBT:CdSe/Au (b). The dashed blue lines are fitted curves based on Child’s law.

results in more favored collection of photogenerated charges as reflected by the increase in \( J_{sc} \) and FF of the EDT-treated PV devices.

The higher level of performance enhancement for the devices with low AR nanorods can be also explained by the improvement in charge transport. Due to their short lengths, charge carriers along nanorods are more prone to be trapped and recombined for the inefficient transport that leads to relatively lower overall device performance.\(^{16}\) Removal of these charge recombination centers upon the EDT
treatment reduces the trapping of the photogenerated charges, thus resulting in more significant impact on the device performance.

The effect of the additives on the device performance can also be attributed to the charge transport. Similar to the EDT treatment, though the ODT treatment can also remove the X-type ligands, its long alkyl chain hinders the electronic interaction and decreases charge transport, thus resulting in low $J_{sc}$ and FF. The X-type ligands are not able to be removed by the DIO treatment. Together with its long alkyl chain, the DIO treatment could more seriously deteriorate the charge transport, as reflected in the device performance of the hybrid PV cells.

**7.7 Surface Chemistry of CdSe Nanorods**

Surface chemistry study enables us to give a clearer picture in a CdSe nanorod. As shown in Figure 7-14, the nanocrystals generally have a composition of a CdSe core, a monolayer of Cd$^{2+}$ shell, and a monolayer of mixed L-type (TOPO, TOP, and TOPSe) and X-type ligands (alkyl phosphonic acids). The L-type ligands bond to the CdSe surfaces through weak van der Waals interaction, while the X-type ligands bond to Cd$^{2+}$ through much stronger Coulombic interactions. In particular, an X-type ligand with a single phosphonic acid group such as TDPA preferentially bonds to Cd cations as a monodentate hydrogen phosphonate, and PPA with two phosphonic acid groups tends to bond Cd cations as bidentate hydrogen phosphonates. The neutral molecule TOPO preferentially binds to the Cd sites through oxygen rather than Se based on the *ab initio* calculation. The preferential facets for TOPO binding are (11\overline{2}0) and (01\overline{1}0) facets, with binding energies of 1.23 eV and 1.37 eV, respectively. These two facets are also the preferential binding facets of PA molecules. The *ab initio* calculation also
indicates that binding of PA molecule to CdSe is much stronger than that of TOPO and this binding is also through the oxygen atoms.

The ligand-exchange interaction in pyridine, as revealed by $^{31}$P NMR, only removes the L-type ligands. Based on the chemical characterization results and the study on the surface chemistry of colloidal nanocrystals by several other groups,\textsuperscript{56, 188-191} we propose the following cleavage mechanism of X-type ligands (phosphonic acid species) from CdSe surface upon the EDT treatment. As shown in Figure 7-15, a free EDT molecule adsorbs to the CdSe surface, bonds weakly with a Cd cation, and weakens the S-H bond in EDT. In a concerted process with the assistance of a Lewis base acetonitrile (also used as the solvent), the adsorbed EDT molecule deprotonates into EDT anions. Third, the strong nucleophilic EDT anion attacks X-type ligand bounded Cd cation (Cd-X), following by replacing X-type ligands and simultaneously the formation of Cd-thiolate. The overall reaction is that alkylphosphonic acid species are exchanged by EDT and Cd$^{2+}$ reacts with EDT to form Cd-thiolate (Figure 7-15). This reaction is a typical nucleophilic substitution reaction.
7.8 Summary

Interface engineering has been demonstrated to be of critical importance in enhancing the performance of organic-inorganic hybrid photovoltaic cells. The power conversion efficiency of the hybrid PV cells based on CdSe nanorods and low-gap polymer PCPDTTBT under AM 1.5 G illumination reaches to a record level of 5% upon EDT treatment, which is comparable to the state-of-the-art organic counterparts using fullerene derivative and PCPDTTBT as the active layer. In general, depending on the conjugated polymers and nanorod size, ~30 – 90% enhancement in $\eta_p$ has been observed for polymer:nanocrystal hybrid PV cells with EDT treatment.
A series of optical, electrical, chemical, and structural characterization have been performed to understand the nature of the EDT treatment on device performance and surface chemistry of CdSe nanocrystals. The results indicate that the EDT treatment results in the removal of the charged X-type ligands and simultaneous passivation of surface defects by the formation of Cd-thiolate, which leads to reduced recombination and charge trapping sites upon the nanocrystal surface and improved electron transport. In addition, the surface chemistry of CdSe nanocrystals after each step of chemical treatment has been depicted; and the reaction mechanism of X-type ligand bounded CdSe nanocrystals with EDT has also been proposed as a nucleophilic substitution reaction.
CHAPTER 8
GRAFTING CONJUGATED OLIGOMERS TO COLLOIDAL NANOCRYSTALS

8.1 Introduction

Chapter 7 strengthens the importance of interface engineering by chemical treatment in achieving high-efficiency organic-inorganic hybrid photovoltaic cells. The development in synthetic chemistry together with the unsaturated surface nature of colloidal nanocrystals makes it possible to directly interface organic donor with inorganic acceptor.\textsuperscript{194-196} As shown in Figure 8-1, such an organic-inorganic bond could be a “center” for direct charge transfer, which may reduce exciton recombination due to the relatively short diffusion length in organic-based system. The molecular interaction among conjugated backbone in organic materials creates a “channel” for efficient hole transport; and the photogenerated electron can be exclusively extracted through the nanocrystal phase.

Direct grafting of organic molecule to colloidal nanocrystals may carry additional advantages compared to the typical ligand-exchange method for removing the alkyl-chain ligands on the nanocrystal surface originated during synthesis. First, the traditional ligand-exchange using small molecules such as pyridine results in the remaining of small molecules upon nanocrystal surface, while the direct grafting only leaves the donor materials. Second, the ligand-exchanged colloidal nanocrystals are typically less dispersible in organic solvents,\textsuperscript{61} which leads to unfavorable phase separation when blended with conjugated polymers; while the organic-grafted nanocrystal is a supermolecule that has similar processing robustness as individual organic molecules. Third, the absorption of either organic or inorganic occurs close to the organic-inorganic interface, which significantly reduces the exciton diffusion path
Figure 8-1. (color) Schematic drawing of colloidal nanocrystals grafted by conjugated oligomers through strong chemical interaction. The grafting enables direct charge transfer at the organic-inorganic interface immediately after exciton generation. The molecular interaction among conjugated oligomers also enables the packing of oligomers to form a hole-transporting channel.

(Figure 8-1). In addition, the anchoring group at the organic-inorganic interface can be tailored to facilitate the charge transfer and transport and reduce recombination traps.

In this chapter, we attempt to engineer the organic-inorganic interface by directly grafting photoactive conjugated oligomers to colloidal nanocrystals. The grafting of oligomers to nanocrystals has been studied by various characterization techniques. Hybrid PV cells based on these oligomer-grafted nanocrystal supermolecules have also been fabricated and evaluated.

8.2 Design and Properties of Functional Oligomers

Though small molecules or oligomers have the advantages of defined chemical and conformational structures and reproducibility, they are generally used in vacuum-deposited organic photovoltaic devices, partly because these small molecules tend to crystallize and/or aggregate, rather than form bi-continuous network with acceptor materials when processed into thin films using wet chemistry. This situation changes as wet chemistry processing approach improves. Recently, organic solar cells based on
small molecule and PC70BM with $\eta_p = 6.7\%$ have been reported using a small percent of solvent additive during the film formation.\[1,7\]

Here we design three monofunctionalized oligomers with defined chemical structure for interfacing with nanocrystals for hybrid PV cells (Figure 8-2).\[1,9,7\] The oligomers are asymmetric conjugated molecules with a phosphonic acid anchoring group at one end, which has the strongest affinity with CdSe nanocrystals in both the theoretical and experimental perspectives (Chapter 7). The energy gaps and HOMO and LUMO levels of the oligomers can be tailored by varying the conjugation degree and nature of the aromatic rings. The OPE-A based on phenylene ethynylene typically has large energy gap, with similar properties to the PPV derivatives. The T6-A based on thiophene mimics the well-known P3HT with good crystallinity, high hole mobility, and lower-gap than OPE-A. The T4BTD-A introduces the donor-accept concept for designing low-gap organic molecules: two electron-rich thiophene groups and one electron-deficient BTD group are linked together through cross-coupling reaction.
Figure 8-3. (color) UV-Vis absorption spectra of functional oligomers and 6 nm CdSe particles.

The UV-visible absorption spectra of the oligomers in solution were shown in Figure 8-3. The oligomers exhibit wide absorption wavelength bands, the peaks of which locate at 323 nm and 379 nm for OPE, 428 nm for T6, and 360 nm and 510 nm for BTD, respectively. The optical gaps of these oligomers, determined based on the onset of the absorption, are relatively large for OPE (2.8 eV) and T6 (2.4 eV); while the gap has been reduced to 2.0 eV for T4BTD due to the energy mixing of the BTD acceptor unit with thiophene donor unit.

Energy levels of the oligomers determined by cyclic voltammetry (CV) and UV-Vis absorption were shown in Figure 8-4. In general, the oligomers have suitable energy levels to form a type-II staggered structure with nanocrystals. Both OPE and T6 show very shallow LUMO levels that could prevent electron leakage from acceptor; while the OPE HOMO is very deep, close to the nanocrystal CB, which may result in significant charge recombination due to hole leakage from OPE to nanocrystals. The HOMO and LUMO levels of T4BTD move downward significantly, while they are still aligned with nanocrystals to create enough energy offset (> 0.3 eV) for charge transfer.
8.3 Oligomer-grafted Nanocrystal Hybrids

The oligomer-grafted nanocrystal hybrids were prepared by mixing oligomers and nanocrystals in solution for 2 h and then purified to remove the un-grafted oligomers through several cycles of dispersion in good solvent (chloroform) and precipitation in poor solvent (methanol). The resulting oligomer:CdSe hybrids have characteristic colors of the oligomers in solution. This grafting was firstly confirmed by thermogravimetric analysis (TGA), as shown in Figure 8-5. The native nanocrystals contain ~18% organic ligands corresponding to the OA and TOPO; while the grafting leads to ~4% – 8% increase in organic content (22%, 26%, and 24% for OPE, T6, and T4BTD, respectively). A higher organic content is likely due to higher molecular weights of oligomers (OPE-A: 815 g/mol; T6-A: 827 g/mol; T4BTD-A: 797 g/mol; OA: 282 g/mol; TOPO: 415 g/mol). However, the degree of ligand-exchange and the unknown distribution of the native ligands upon nanocrystal surface make it difficult to quantitatively estimate the number of oligomers based on TGA results.
Fluorescence quenching experiments were also carried out to monitor the grafting.\textsuperscript{197,198} Fluorescence of oligomers with a phosphonic acid group can be rapidly quenched with addition of CdSe nanocrystals and vice versa (Figure 8-6); while the FL quenching of oligomers with an ester group is less efficient by adding nanocrystals or vice versa (Figure 8-6). It is also suggested, due to the dual FL quenching of OPE-A:CdSe and T6-A:CdSe, the quenching occurs via a charge-transfer process rather than direct energy-transfer. Through FL quenching experiments, it can be estimated that each nanocrystal has been covered by ~50 conjugated oligomers.

Transmission electron microscopy is also employed to study the oligomer-CdSe grafting. As shown in Figure 8-7, the native nanocrystals are monodisperse in size and uniformly distributed; while the oligomer-grafted-nanocrystals tend to aggregate, which may be due to the strong intermolecular interaction of oligomers among neighboring nanocrystals.
Figure 8-6. (color) Evolution (a) of the fluorescence of OPE-E and OPE-A upon addition of CdSe NPs into the solution, and evolution (b) of the peak fluorescence intensities for the ester (squares) and acid (circles) forms of OPE (black line), T6 (blue line) and T4BTD (red line) upon incremental addition of CdSe NCs.

8.4 Oligomer-grafted-nanocrystal Hybrid Photovoltaic Cells

To test the validity of the oligomer-grafting nanocrystal hybrids for photovoltaic application, we then fabricated oligomer:CdSe hybrid PV cells. The hybrids were spin-coated from CF solution with a thickness ~60-80 nm and then a ZnO NP layer was deposited to smoothen the active layer, prevent hole leakage, facilitate electron extraction, and manage light absorption as suggested in Chapter 5 and Chapter 6. The active layer and the ZnO layer were co-annealed at 150 °C for 30 min at a glove box before Al deposition. The final device structure was shown in the inset of Figure 8-8a.

The photovoltaic effect has been observed for all oligomer:CdSe cells, and the $J$ – $V$ characteristics of the oligomer:CdSe cells are shown in Figure 8-8a. The OPE:CdSe cell show a $J_{sc}$ of 0.3 mA/cm$^2$, $V_{oc}$ of 0.41 V, and $\eta_p$ of 0.03%. The low $J_{sc}$ is likely and partly due to the narrow absorption wavelength range of OPE and relatively low absorption coefficient of CdSe nanocrystals. The $J_{sc}$ has been increased when a
lower gap oligomer T6 was used, while the T6:CdSe cell shows very small $V_{oc}$ (0.29 V), which may result from unfavorable large phase separation of the hybrid. The low-gap oligomer T4BTD leads to the further increasing in $J_{sc}$ and a high $V_{oc}$ (0.68 V) has been observed in this cell, suggesting promising photovoltaic application of the T4BTD:CdSe hybrid system if the processing conditions were optimized.

The EQE of these oligomer:CdSe cells were also collected and shown in Figure 8-8b. The OPE:CdSe cell shows two EQE peaks of 10% at $\lambda = 350$ nm and of 7% at $\lambda = 374$ nm that corresponds to the OPE absorption. The EQE at $\lambda > 450$ nm is low (< 5%), and a small shoulder at $\lambda = 640$ nm is due to the contribution of nanocrystal absorption. The EQE of the T6:CdSe cell is much broader and higher than the OPE cell; and the EQE at 400 nm < $\lambda$ < 550 nm is likely contributed from the T6 absorption. The T4BTD:CdSe cell exhibits the broadest and highest EQE. The two EQE bands centered at 370 nm and 505 nm correspond to the T4BTD absorption. Again, a small shoulder at
Figure 8-8. (color) $J - V$ characteristics (a) under 1 sun AM 1.5G illumination and EQE (b) of hybrid PV cells based on oligomers-grafted nanocrystals.

$\lambda = 640$ nm is also observable for the contribution of nanocrystal absorption. In brief, both oligomers and CdSe nanocrystals contribute to the photocurrent generation in all oligomer-grafted CdSe hybrid solar cells.

The efficiencies of these oligomer:CdSe cells are much lower than their polymer counterparts (Chapter 5). The absorption coverage could be a significant issue for the lower efficiencies, particularly for OPE and T6-based cells. However, the T4BTD cell has similar absorption coverage to the P3HT and PB$_n$DT cells. In fact, the oligomer:CdSe hybrid morphology may be the main reason for the such low performance. As shown in Figure 8-9, the T4BTD:CdSe hybrid film shows several large aggregation domains (> 300 nm in parallel length, and vertically > 150 nm). This
significant aggregation is detrimental for exciton dissociation and charge carrier extraction. Hence, processing is still an issue for high-efficiency hybrid PV cells using small molecules as donor materials.

### 8.5 Summary

In this chapter we demonstrate the direct interfacing of CdSe nanocrystals by conjugated oligomers. Three conjugated oligomers bearing a phosphonic acid group were designed with different energy gaps and energy levels. The TGA, PL quenching, and TEM study clearly indicate that the oligomers are intensively grafted to the CdSe nanocrystal through a strong chemical interaction (likely covalent). Though the oligomer:CdSe hybrid PV cells exhibit photovoltaic effect as reflected in $J-V$ measurement, the efficiencies of these cells are relatively low at this moment. The EQE shows that both oligomers and CdSe nanocrystals contribute to the photogeneration. High-performance PV cells based on oligomer-grafted CdSe hybrids is anticipated if the
processing could be improved and the anchoring group could be more systematically investigated.
CHAPTER 9
SOLUTION-PROCESSED METAL OXIDE ANODE INTERLAYER

9.1 Introduction

The relative low work function and rough surface of indium tin oxide (ITO) substrate typically require an exotic interlayer that facilitates the charge injection/extraction in organic-based photovoltaic cells. Due to its high conductivity, high transparency, low-temperature aqueous solution processing, and commercial availability, PEDOT:PSS has witnessed great success as anode interlayer during the progress of organic-based solar cells. However, an increasing number of studies reveal the hygroscopic and acidic nature of the PEDOT:PSS is one of the main causes of device degradation.\(^{173}\) Plus, the relatively low work function (~5.0 eV) makes PEDOT:PSS not the ideal choice for organic solar cells using organic semiconductors with deep HOMO level.

Theoretically, an ideal anode interlayer material may include the following characteristics: i). proper energy level alignment with donor materials for charge injection/extraction; ii). high transparency and conductivity to reduce photocurrent loss; iii). comparability with roll-to-roll fabrication technique; iv). structural and chemical robustness to avoid inhomogeneous chemical composition and morphology; and v). chemically stable and environmentally friendly.

Transition metal oxides (TMOs), including molybdenum oxide (MoO\(_3\)), nickel oxide (NiO), vanadium oxide (V\(_2\)O\(_5\)), and tungsten oxide (WO\(_3\)), have then arisen as promising anode interlayer candidates.\(^{136, 137, 199-203}\) These TMOs are transparent in visible to near-infrared spectrum region, electrically conductive due to chemical non-stoichiometry, and chemically and structurally stable in ambient condition. However,
these TMOs are typically deposited upon ITO substrates at high temperature (> 400 °C) and at high-vacuum,\textsuperscript{199-202} which complicates the device fabrication and incompatible with roll-to-roll processing. Recently, MoO\textsubscript{x} thin film prepared by solution processing at relatively low temperature (< 200 °C) has been reported by several groups.\textsuperscript{204-208} These MoO\textsubscript{x} films are either prepared in the form of nanoparticle precursor or converted from molybdenum oxide precursors. NiO precursor nanoparticles can be also prepared from solution chemistry, but they require relatively high temperature (> 400 °C) to convert these precursor nanoparticles into NiO thin films.\textsuperscript{209, 210} Tungsten oxide that is less harmful to the environment than other TMOs has received less attention using solution processing,\textsuperscript{204} though it has been extensively studied in organic solar cells using vacuum deposition.\textsuperscript{201}

In this chapter, we demonstrate the low-temperature solution processing of tungsten oxide interlayer for organic-based photovoltaic cells. The solution-processed tungsten oxide films are very smooth, highly transparent, and morphologically amorphous. The organic PV devices using solution-processed tungsten oxide as anode interlayer show comparable efficiency to those based on archetypal PEDOT:PSS and other anode interlayer.

\textbf{9.2 Synthesis and Characterization of Tungsten Oxide Precursor and Thin Film}

\textbf{9.2.1 Synthesis of Tungsten Oxide Precursor}

Tungsten oxide precursor solution was prepared by dissolving a saturated amount (\sim 22 mg/mL at room temperature) of ammonium tungsten oxide hydrate ((NH\textsubscript{4})\textsubscript{10}H\textsubscript{2}W\textsubscript{12}O\textsubscript{42}·4H\textsubscript{2}O, here denoted as source material, Alfa Aesar) in deionized water and stirred for 1 h at 80 – 90 °C at air. A clear aqueous solution was obtained after cooling to room temperature, and not any other treatment is needed. The saturated
precursor solution can be directly diluted by deionized water at room temperature to obtain precursor solution with various concentrations. 3 nm, 6 nm, and 10 nm thin films were prepared by spin-coating tungsten oxide precursor solutions with concentrations of 6 mg/mL, 11 mg/mL, and 22 mg/mL, respectively, at 5000 rpm for 1 min. The precipitated crystals of ammonium tungsten oxide hydrate (here denoted as precipitated crystal) were collected from an aqueous solution containing over-saturated ammonium tungsten oxide at room temperature. Before thermogravimetric analysis (TGA) measurement, the precipitated crystals were naturally dried at room temperature for a few days. This drying is supposed to lose some crystalline water molecules incorporated during dissolution at elevated temperature.

9.2.2 Characterization of Tungsten Oxide Thin Film

The tungsten oxide solution was spin-coated upon soda-lime glass for transmittance and X-ray diffraction (XRD) measurement, upon ITO substrates for atomic force microscopy (AFM) measurement, and upon Si substrates for X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and thickness measurements. All thin films were thermally annealed at 150 °C for 30 min. The surface morphologies of thin films and ITO substrate were carried out in a Veeco Nanoscope scanning probe microscopy operating in a tapping-mode. XRD measurement was carried out in an X’Pert powder X-ray diffractometer using Cu Kα radiation and operating at 40 kV and 45 mA. Thermogravimetric analysis was carried out in a TGA Q5000 at a heating rate of 5 °C at the air. The thickness of tungsten oxide thin film was determined by an ellipsometer based on a Cauchy model.
Figure 9-1. (color) TGA of ammonium tungsten oxide bulk materials.

**9.3 Solution-processed Tungsten Oxide Thin Film**

Tungsten oxide precursor solution was prepared by dissolving ammonium tungsten oxide in deionized water at 80 °C. The resulting solution is transparent, colorless, and stable in ambient condition, which has not shown any change in color and transparency after storage for over half a year. This dissolution process is not intended to thermally decompose the ammonium tungsten oxide into tungsten oxide, but rather, to disperse it in aqueous solution as tungsten oxide precursor. TGA result of precipitated crystal from the precursor solution indicates the precursor in aqueous solution retains the chemical stoichiometry (Figure 9-1). Also, the pH value of the aqueous solution before and after dissolution of ammonium tungsten oxide precursor remains neutral, indicating there is no or limited ionization occurring.

TGA thermogram of ammonium tungsten oxide hydrate crystal precipitated from its precursor solution shows that it starts to decompose at a very low temperature and dehydration occurs at ~50 °C (Figure 9-1), which is due to the excess incorporation of
water molecules to starting source material. The TGA thermogram of ammonium tungsten oxide hydrate source material shows a delayed behavior, where complete dehydration of absorbed water molecules occurs at ~160 °C and with a ~40 °C stage. After initial dehydration, the precipitated crystal shows a gradually thermal decomposition behavior at 50 – 300 °C where the excess water molecule and ammonium are removed, while the source material exhibits a sharp decomposition behavior at this temperature regime. This suggests the incorporation of water molecule restructures the ammonium tungsten oxide framework. At temperature > 400 °C, further dehydration occurs for both samples to yield a stable and stoichiometric tungsten oxide (WO₃). The early decomposition behavior of precipitated crystal also suggests the possibility of decomposing the precursor thin film into tungsten oxide at an even lower temperature due to dimension reducing.

X-ray photoelectron spectroscopy was used to study the chemical states of tungsten oxide based thin films thermally treated at various temperatures. As shown in Figure 9-2, the O 1s spectra of the thin films were gradually shifted to lower-binding energies as annealing temperature increased. The film annealed at 100 °C shows two O 1s peaks locating both at 532.0 eV that corresponds to ammonium tungsten oxide as indicated in the non-annealed sample and at 530.5 eV that corresponds to tungsten oxide as demonstrated in the samples annealed at 150 °C and 200 °C. The W 4f spectra of these films also show a slight shift in binding energy as annealing temperature increases, and the binding energies at 37.7 eV and 35.6 eV corresponds to the characteristic W⁶⁺ 4f 5/2 and 7/2 of tungsten oxide. Other than W⁶⁺, there is no W state revealed in the XPS spectra for all the tested samples, which is also proved by the
The fact that film color did not show any visible variation during annealing. In particular, the intensity of W 4f spectra significantly increases for the annealed samples, suggesting the shrink of precursor thin film and making W more sensitive for X-ray electron penetration. Integration of the intensity of O 1s and W 4f spectra reveals the sample annealed at ≥150 °C has an O/W of (2.9-3.1)/1. The slight non-stoichiometric composition may be due to the incomplete decomposition of water molecule at relatively low temperature (≤ 200 °C) and to oxygen deficiency under annealing at the inert condition.

We further probed the morphological structure of these thin films prepared with different annealing temperature by X-ray diffraction. The annealed thin film shows
almost the same XRD pattern as the non-annealed precursor thin film and not any identical sharp peak appears (Figure 9-3), suggesting the amorphous nature of these tungsten oxide thin films. Being amorphous could be of benefit for organic electronics, since the device performance will not be limited by the spatial/structural non-uniformity.\textsuperscript{201}

![XRD pattern graph]

Figure 9-3. (color) XRD patterns of tungsten oxide precursors annealed at different temperature.

Surface morphology of tungsten oxide thin films deposited upon ITO substrates was probed by tapping-mode AFM. Figure 9-4a & 9-4b show the AFM images of 3 nm and 10 nm WO\textsubscript{3} films deposited upon ITO substrates, respectively. The 3 nm film shows some grains, while these grains have size much smaller than those of ITO (Figure 9-4c). Such a thin film may not fully cover the ITO surface and more likely fill its pin-holes, which thus leads to significant reduction in the root-mean-square roughness ($R_{\text{rms}}$) from 1.7 nm for ITO to 0.82 nm for ITO with a 3 nm WO\textsubscript{3} film. The 10 nm WO\textsubscript{3} film is very homogeneous and does not show any grains, pin-holes, or microstructures, which
Figure 9-4. (color) Tapping mode AFM topological images of (a) ITO with a 3 nm WO$_3$, (b) ITO with a 10 nm WO$_3$, (c) bare ITO substrate, and (d) ITO with a 20 nm PEDOT:PSS layer. The root-mean-square roughness ($R_{\text{rms}}$) of sWO$_3$ (3 nm), sWO$_3$ (10 nm), ITO, and PEDOT:PSS are 0.82 nm, 0.34 nm, 1.7 nm, and 1.0 nm, respectively.

results in a very smooth surface with $R_{\text{rms}} = 0.34$ nm, even smoother than those vacuum-deposited WO$_3$ films. Such a smooth surface, as suggested by the XRD result, is due to the amorphous nature of WO$_3$ thin film. As a comparison, PEDOT:PSS, the typical anode interlayer for organic solar cells, has an $R_{\text{rms}}$ of 1.0 nm deposited upon ITO substrate (Figure 9-4d).

Transparency is another important factor of anode interlayer in organic electronics. Figure 9-5 shows the transmittance of different thin films deposited upon soda-lime glass. The transmittance of the tungsten oxide thin film follows exactly with the sola-lime glass at the entire wavelength region, with transmittance > 90% at $\lambda < 800$ nm for 3 nm film and at $\lambda < 700$ nm for 10 nm film and transmittance > 88% at the entire
Figure 9.5. (color) Transmittance of various interlayers deposited upon glass substrates. Compared to 20 nm PEDOT:PSS deposited upon glass, 10 nm WO₃ film shows 3-6% higher transmittance, particularly at λ > 700 nm, suggesting the additional advantage of WO₃ as anode interlayer in organic solar cells utilizing low-gap small molecules / polymers as light-harvesting materials.

9.4 PV Devices with Tungsten Oxide Anode Interlayer

9.4.1 Solution-processed Polymer Solar Cells

The chemical, morphological, and optical properties of the solution-processed tungsten oxide thin films suggest much promising as anode interlayer and/or charge recombination layer in organic solar cells. As a proof, we first demonstrated polymer solar cells using archetypal P3HT:PCBM as the active layer. In order to maximize device performance, the PEDOT:PSS and WO₃ thin films were all annealed at 150 °C before active layer deposition. The J–V characteristics of the P3HT:PCBM devices were shown in Figure 9-6 and their photovoltaic performance parameters were summarized in Table 9-1.
The device using bare ITO shows high injection barrier and series resistance (17 Ω·cm²), resulting in low photocurrent and voltage. However, introducing an ultrathin 3-nm WO₃ film as anode interlayer into P3HT:PCBM device drastically decreases series resistance to 5.6 Ω·cm², and the device shows short-circuit current $J_{sc} = 8.0$ mA/cm², open-circuit voltage $V_{oc} = 0.621$ V, fill factor FF = 0.56 and ultimate $\eta_p = 2.8\%$, all of which are analogous to the device using PEDOT:PSS as an anode interlayer ($J_{sc} = 8.3$ mA/cm², $V_{oc} = 0.633$ V, FF = 0.56, and $\eta_p = 2.9\%$). Slightly increasing film thickness to 6 nm and 10 nm, the WO₃ devices show exactly the same $J_{sc}$ as the PEDOT:PSS device but slightly higher $V_{oc}$ due to lower dark current (Figure 9-6a). In particular, FF has been significantly increased from 0.55 to 0.61 probably due to more balanced charge injection and collection, resulting in enhancement in $\eta_p$ from 2.9% of the PEDOT:PSS device and 2.8% of the sMoOₓ device to 3.2% of the 10-nm WO₃ device (Table 9-1). This efficiency is also comparable to the state-of-the-art P3HT:PCBM devices using either vacuum-deposited or solution-processed TMOs anode interlayers reported by other groups. Moreover, as shown in Figure 9-6a, the dark current of the WO₃ devices has been drastically decreased compared to the devices using either bare ITO or PEDOT:PSS, suggesting effective blocking in leakage current.

The EQE as a function of wavelength has also been recorded for the P3HT:PCBM devices using various anode interlayers. As shown in Figure 9-6c, the devices with an anode interlayer show much higher EQE at all the photoresponsive regime. The WO₃ devices exhibit slightly higher EQE than the PEDOT:PSS device at 420 nm < $\lambda$ < 570 nm, which is likely due to the higher transparency of the WO₃ films.
The device performance has also been found to be dependent on the annealing temperature of the tungsten oxide film. As shown in Figure 9-7, the device using WO$_x$ films without annealing exhibits an S-shape of $J - V$ characteristic and results in low $J_{sc}$ and FF, which is largely due to the high series resistance ($33 \, \Omega \cdot \text{cm}^2$) rising from...
Table 9-1. Summary of photovoltaic performance under 1 sun AM 1.5 G illumination for P3HT:CdSe hybrid photovoltaic cells.

<table>
<thead>
<tr>
<th>Anode interlayer</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta_p$ (%)</th>
<th>$R_s$ (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare ITO</td>
<td>6.9</td>
<td>0.492</td>
<td>0.32</td>
<td>1.1</td>
<td>17</td>
</tr>
<tr>
<td>PEDOT:PSS (20 nm)</td>
<td>8.3</td>
<td>0.633</td>
<td>0.56</td>
<td>2.9</td>
<td>3.9</td>
</tr>
<tr>
<td>sWO$_3$ (3 nm)</td>
<td>8.0</td>
<td>0.621</td>
<td>0.56</td>
<td>2.8</td>
<td>5.6</td>
</tr>
<tr>
<td>sWO$_3$ (6 nm)</td>
<td>8.3</td>
<td>0.639</td>
<td>0.59</td>
<td>3.1</td>
<td>4.3</td>
</tr>
<tr>
<td>sWO$_3$ (10 nm)</td>
<td>8.3</td>
<td>0.641</td>
<td>0.61</td>
<td>3.2</td>
<td>4.2</td>
</tr>
<tr>
<td>sMoO$_x$ (10 nm)*</td>
<td>8.1</td>
<td>0.612</td>
<td>0.56</td>
<td>2.8</td>
<td>3.0</td>
</tr>
</tbody>
</table>

* sMoO$_x$ was prepared based on reference 206 at ambient condition.

insulating nature of the ammonium tungsten oxide precursor interlayer prepared at room temperature. When the annealing temperature increased to 50 °C, the device’s series resistance was reduced by 75% to 8.0 Ω·cm$^2$ due to the partial decomposition of the tungsten oxide precursor, correspondingly resulting in better $J_{sc}$ (6.3 mA/cm$^2$) and FF (0.49). The device performance has been further increased to the best values with $J_{sc} = 9.0$ mA/cm$^2$, $V_{oc} = 0.639$ V, FF=0.58, and $\eta_p = 3.3\%$ when the tungsten oxide film annealed at 150 °C, at which the series resistance has been reduced to ~ 4-5 Ω·cm$^2$. Further increasing annealing temperature to 200°C results in an S-shape in $J–V$ characteristic due to the increased series resistance (7.1 Ω·cm$^2$) and consequently the device performance has been significantly reduced. This increased series resistance probably contributes from the oxygen deficiency in ITO or tungsten oxides during annealing. In brief, the chemical composition of the tungsten oxide film is highly dependent on the annealing temperature, which in turn reflects in the device series resistance and efficiency.
Figure 9-7. (color) Effect of annealing temperature of WO$_3$ interlayers on the performance of P3HT:PCBM solar cells.

9.4.2 Vacuum-deposited Small-molecule Solar Cells

The vacuum growth of organic small molecule thin film has been regarded to be highly dependent on substrate’s physical properties such as crystallinity, lattice orientation, and domain size, which in turn affects the performance of the PV cells.$^{212}$ As discussed, tungsten oxide film deposited upon ITO substrate is very smooth and transparent, which may be of benefit for the growth of organic molecules and then their respective electronic devices.

We first demonstrate the robustness of the tungsten oxide film in bilayer CuPc/C60 cell. As shown in Figure 9-8a, the device deposited upon pure ITO shows $J_{sc} = 3.8$ mA/cm$^2$, $V_{oc} = 0.48$ V, FF = 0.60, and $\eta_p = 1.1\%$; while the devices with a WO$_3$ layer show slightly increased $J_{sc} = 4.1$ mA/cm$^2$ and $V_{oc} = 0.51$ V but similar FF = 0.60, resulting in $\sim 18\%$ enhancement in $\eta_p$ (1.3%). The enhancement in $V_{oc}$ attributes to the suppression of dark current when a WO$_3$ layer included, and the increase in $J_{sc}$ is likely due to better hole extraction. As shown in Figure 9-8b, the EQE further confirms the
increase in $J_{sc}$. The device with a WO$_3$ layer shows higher EQE at 550 nm $< \lambda < 700$ nm that mainly contributes from CuPc absorption, suggesting photogenerated hole can be more efficiently extracted when dissociated at the CuPc – C60 interface.

Figure 9-8. (color) Effect of a WO$_3$ interlayer on the bilayer CuPc/C60 solar cells. (a, b) J – V characteristics under 1 sun AM 1.5G illumination and dark condition; (c) the corresponding EQE.

The effect of an anode interlayer may be more prominent in device using deep-HOMO molecules. In order to prove the universality of the solution-processed tungsten oxide thin film, we fabricated mixed-planar SubPc:C60 (1:4)/C60 cells. As shown in Figure 9-9, the devices with a WO$_3$ layer show an increased $V_{oc}$ ($\sim$0.08 V), while $J_{sc}$ and FF remain the same as the device directly deposited upon the ITO substrate. This
enhancement in $V_{oc}$ is again due to more than one order of magnitude decrease of dark current (Figure 9-9a).

Figure 9-9. (color) Effect of a WO$_3$ interlayer on the mixed-planar SubPc:C60/C60 solar cells. (a, b) $J$ – $V$ characteristics under 1 sun AM 1.5G illumination and dark condition.

9.5 Summary

In this chapter we demonstrate the low-temperature solution-processing of tungsten oxide thin films and their application in organic photovoltaic cells. The XPS and TGA studies indicate that the solution-processed tungsten oxide precursor has been converted to tungsten oxide after annealing at a mild temperature (150 °C). The
resulting tungsten oxide film is very smooth, transparent, and amorphous, which are the very characteristics as anode interfacial layer for organic-based solar cells.

The tungsten oxide film as anode interlayer has been firstly demonstrated in polymer solar cells. The P3HT:PCBM cell with a WO3 layer shows comparable or even better device performance compared to the cell using PEDOT:PSS interlayer. In particular, the FF of the cell with WO3 layer has been significantly increased from 0.56 to 0.61, suggesting that the WO3 layer may facilitate charge extraction. The polymer solar cells also exhibit annealing temperature dependent performance of the WO3 layer, which is due to and an indicator of the conversion efficacy of tungsten oxide precursor to tungsten oxide.

The tungsten oxide interlayer also shows robustness in organic-based solar cells, which is also applicable in vacuum-deposited small-molecule solar cells. Using a 3 nm – 10 nm WO3 interlayer, both the bilayer CuPc/C60 cell and the mixed-planar SubPc:C60/C60 cell show slightly increased $J_{sc}$ and $V_{oc}$, resulting in ~ 10-20% enhancement in $\eta_p$. 
CHAPTER 10
CONCLUSIONS AND FUTURE WORK

10.1 Conclusions

Though organic-inorganic hybrid photovoltaic cells containing colloidal nanocrystals have shown significant advance, the pace is in a slower manner compared to that of all-organic counterparts, partly because it involves much more complicate electronic, chemical, and morphological interfaces. This dissertation devotes to better understanding the fundamental chemical and physical properties of organic-inorganic hybrid materials, and their relationship with developing high-performance organic-inorganic hybrid photovoltaic cells. In particular, by tailoring both conjugated polymers and colloidal nanocrystals, engineering polymer-nanocrystal interface, and optimizing device architecture, the power conversion efficiency of bulk heterojunction organic-inorganic hybrid PV cells has been increased from 1-3% in literature to 3-5% present in this dissertation (Figure 10-1).115

10.1.1 Organic-inorganic Hybrid Materials

Colloidal inorganic nanocrystals can be designed and tailored in the perspective of structure and properties such as the size, shape, composition, and surface chemistry. First, as shown in Chapter 4, the hybrid PV cells show performance dependence on nanoparticle size, which attributes to increased electron mobility and decreased surface defect density as nanoparticle size increases. Second, hybrid PV cells also show an aging effect as exposed to the air, attributing to the interaction between CdSe surface with moisture / oxygen and also suggesting the complex surface property of colloidal nanocrystals. Moreover, compared to spherical nanocrystals, the elongated counterparts show enhanced performance in hybrid PV cells, which is due to the
Figure 10-1. (color) The plot of power conversion efficiency ($\eta_p$) vs year in bulk-heterojunction organic-inorganic hybrid photovoltaic cells. This plot summarizes the major advance, and the champion efficiencies of hybrid PV cells in other groups based on each kind of colloidal nanocrystals have also been shown. The data for other groups' work is derived from reference 17, 18, 115, and 146. The black and red curves are the eye guiders of the progress in this field for both other groups' work and this work, respectively. The dashed red line indicates the starting date of this work.

increased charge transport property in hybrid matrix. In addition, composition-varied cadmium chalcogenides nanorods were also designed and synthesized. The initial result shows hybrid PV cells based on CdS nanorods and P3HT are promising for further investigation.

Tailoring both energy gap and energy levels of colloidal nanocrystals, to a large extent, is constrained to their intrinsic properties of bulk materials; while conjugated polymers are more feasible and not limited to starting organic unit or group. The archetypal P3HT has been mostly demonstrated as donor materials in hybrid PV cells,
while its relatively-large energy gap (1.9 eV) limits the photon harvesting that leads to relatively low short-circuit current ($J_{sc} \sim 5 - 6 \text{ mA/cm}^2$) and narrow spectral response (~650 nm). Besides, its energy levels are not optimally aligned with those of colloidal nanocrystal to maximize open-circuit voltage. In chapter 6, a low-gap polymer PCPDTBT that extends spectral response to ~850 nm was utilized as donor materials for hybrid PV cells, resulting in enhanced $J_{sc}$ due to the photocurrent contribution from near-infrared region. The optimized device using PCPDTBT and CdSe nanoparticles shows $J_{sc} \sim 9 \text{ mA/cm}^2$ and $\eta_p 3.5\%$. Moreover, the open-circuit voltage of hybrid PV cells can also be manipulated by choosing conjugated polymer with optimal energy level alignment with nanocrystal acceptor. This was demonstrated using a polymer PBnDT-FTAZ with deep HOMO level (~5.36 eV), resulting in hybrid PV cells with open-circuit voltage as high as 0.9V and $\eta_p > 3\%$ (Chapter 6).

The processing of organic-inorganic hybrid materials also has a vast impact on the device performance. As discussed in chapter 6, the domain size and surface roughness of PCPDTBT:CdSe hybrid films have shown to be highly dependent upon processing solvents, which in turn affects the hybrid PV cell performance. Thermal annealing that may further lead to optimal phase segregation and removal of exciton and charge carrier recombination/trap centers present on CdSe nanocrystals has shown to be an effective manner to enhance the device performance as demonstrated in both P3HT:CdSe and PCPDTBT:CdSe cells.

### 10.1.2 Organic-inorganic Interface

Surface property of colloidal nanocrystals has been found to be of particular importance in bulk-heterojunction organic-inorganic hybrid PV cells, as demonstrated in Chapter 7 and Chapter 8. A significant improvement in performance of hybrid PV cells...
using CdSe nanorods and conjugated polymers has been observed by engineering the polymer-CdSe interface with the EDT treatment. The devices with the EDT treatment show ~30-90% enhancement in $\eta_p$ depending on the aspect ratio of CdSe nanorods, resulting in maximum $\eta_p$ ~3% for P3HT:CdSe cells and record $\eta_p$ ~5% for PCPDTBT:CdSe cells under AM 1.5G illumination, respectively.

Surface chemistry of CdSe nanorods with various chemical treatments was probed by FTIR, NMR, and XPS characterizations. These characterizations unanimously indicate that the ligand-exchange in pyridine selectively removes neutral L-type ligands such as TOPO yet the EDT treatment removes charged X-type ligands such as alkylphosphonic acids and concomitantly passivates the nanocrystal surface by formation of Cd-thiolate. The removal of potential exciton and charge carrier recombination sites together with increased electron mobility of hybrid thin film upon X-type ligand cleavage are the very nature of performance enhancement in hybrid PV cells.

The chemical characterization also further proves the chemical composition of colloidal nanocrystals: a CdSe core with a monolayer of Cd$^{2+}$ and a monolayer of mixed L-type and X-type ligands. The neutral L-type ligands bond to the CdSe surface through dative interaction, and the charge X-type ligands bond to the Cd$^{2+}$ through ionic interaction. Finally, the reaction mechanism between Cd-X-ligand and EDT has also been regarded as a nucleophilic reaction.

The unsaturated surface of colloidal nanocrystals enables to directly interface with organic donor molecules to generate organic-inorganic hybrid supermolecules. Oligomers bearing a chemically-reactive phosphonic acid group were designed and
synthesized. Various chemical, optical, and morphological characterizations demonstrated that the oligomers are bounded to the CdSe surface through strong chemical interaction, resulting in stable oligomer:CdSe hybrid supermolecules and substantial energy transfer between oligomer and CdSe nanocrystal under optical stimulus. The hybrid PV cells based on these oligomer:CdSe nanocrystal hybrid supermolecules showed significant photovoltaic effect and also photocurrent contribution from both oligomers and CdSe nanocrystals.

10.1.3 Semiconductor – Metal Interface

Semiconductor-metal interface is another aspect that can be optimized in an organic-inorganic hybrid PV cell. Introducing an interlayer to the anode or cathode is the typical strategy to engineer the semiconductor-metal interface (device structure) to facilitate charge injection/extraction and manage light absorption distribution.

Hybrid PV cells using CdSe nanoparticles with a ZnO NP layer show ~30-90% enhancement in $\eta_p$ depending on the nanoparticle size and conjugated polymers, which leads to maximum $\eta_p$ 2.4% for P3HT:CdSe cells and 3.5% for PCPDTBT:CdSe cells under simulated 1 sun AM 1.5G illumination as discussed in Chapter 5 and Chapter 6. The morphological, electronic, and optical studies indicate the ZnO NP layer could optimally re-distribute the optical field within the active layer, smoothen the active layer to provide better contact with the Al cathode, block the hole transport to the cathode, facilitate the electron extraction, and also prevent the exciton recombination at the active layer-Al interface. In addition, the ZnO layer also physically isolates or retards the permeation of moisture / oxygen from cathode side, which leads to dramatic improvement in device environmental stability with ~70% $\eta_p$ retained after storage at the ambient condition for > 2 months.
On the other hand, anode modification has also received much attention for organic-based photovoltaic cells. Though PEDOT:PSS has shown much success in solution-processed polymer solar cells, the intrinsic acidity and hygroscopicity make it detrimental to device stability. In chapter 9, tungsten oxide, one of the less harmful transition metal oxides, has been prepared by converting its precursor by annealing at mild temperature. Various characterizations indicate the solution-processed tungsten oxide thin film is smooth, transparent, and structurally amorphous. The tungsten oxide thin film has been demonstrated as anode interlayer in both solution-processed P3HT:PCBM cells and vacuum-evaporated small molecule cells. The P3HT:PCBM cells show similar $J_{sc}$ and $V_{oc}$ but increased FF compared to the device using PEDOT:PSS, suggesting the tungsten oxide interlayer facilitates charge extraction. In addition, the bilayer CuPc/C60 and mixed-planar SubPc:C60/C60 devices show slightly increased $J_{sc}$ and $V_{oc}$ compared to the devices deposited upon bare ITO substrates.

**10.2 Future Work**

Although bulk-heterojunction organic-inorganic hybrid photovoltaic cells have witnessed significant progress in the past several years, further research effort is still needed to move this technology into commercial interest. Hence, the theme for future work is again to improve the power conversion efficiency of hybrid PV cells to $>10\%$ and device environmental stability $>5$-10 years. Moreover, the study in organic-inorganic hybrid materials can also be extended to the optoelectronic devices such as light-emitting diodes, photodetector, etc.
10.2.1 Organic-inorganic Hybrid Materials

10.2.1.1 Colloidal nanocrystals

Though ZnO, CdS, PbS, etc. have shown some success, so far CdSe is still the mostly-investigated nanocrystals as acceptor in hybrid PV cells, partly because of its maturity in synthesis, better energy level alignment with conjugated polymers, and suitable energy gaps. Nonetheless, the most efficient hybrid PV cells based on CdSe nanocrystals only show $J_{sc} \sim 12 \text{ mA/cm}^2$, $V_{oc} \sim 0.7 - 0.8 \text{V}$, and FF $\sim 0.50 - 0.55$. There is still much room to improve the photovoltaic performance by tailoring colloidal nanocrystals. The ideal colloidal nanocrystals for hybrid PV application may include the following chemical and physical properties: high electron mobility ($\sim 10^{-2}-10^{-3} \text{ cm}^2/\text{Vs}$), energy gap $\sim 1.2-1.5 \text{ eV}$, LUMO level $\sim 3.7-4.0 \text{ eV}$, few surface defects, and flexible surface chemistry.

Colloidal nanocrystals with anisotropic structure have been shown higher electron transport behavior, which have been frequently demonstrated in literature and in this work as well. Aligning elongated nanocrystals vertically upon the substrates could be another strategy to improve the electron mobility of colloidal nanocrystals within a polymer:nanocrystal matrix. Besides, exploring a new approach to passivate nanocrystal surface is also of critical importance in improving electron transport, as exemplified in chapter 7.

Though the natural semiconductors are limited, synthetic chemistry enable to develop nanocrystals non-existed in nature. Alloying two or more semiconductors to produce ternary or quaternary nanocrystals is a choice to optimize energy level and energy gap for PV application based on donor-acceptor heterojunction. Band gap and composition engineering on a nanocrystal (BCEN) as proposed by Peng, is the very
concept for the future development of colloidal nanocrystal for PV application and beyond.

Engineering surface property of colloidal nanocrystals, as demonstrated in chapter 7, is critical in hybrid PV application. The early study in nanocrystal surface tailoring including this work is still in its fancy and requires much more study. Other than organic capping molecules, inorganic ligands as demonstrated in field-effect transistor or organic and inorganic hybrid ligands may also be promising to passivate the nanocrystal surface for hybrid PV cells. The physical mechanism in enhancing the photovoltaic performance by surface passivation also needs more study.

10.2.1.2 Organic semiconductors

Thus far, the organic semiconductors in hybrid PV cells are mostly directly borrowed from study in all-organic solar cells such as P3HT, PCPDTBT, PBnDT, etc. There are very few organic molecules (the functional oligomers in Chapter 7) specially tailored hybrid PV cells. The concept for designing organic semiconductors for hybrid PV cells is more or less similar to that for all-organic PV cells. The energy gap, energy level, hole mobility, and solvent affinity (processability) are the parameters featured in designing organic semiconductor for BHJ PV application. Other than that, organic semiconductors with a reactive group may be advantage for blending with colloidal nanocrystals. This reactive group could not be a charge or exciton sink, but must bind to colloidal nanocrystals through strong chemical interaction. Phosphonic acid (PA) group may be not an ideal choice, since the bonding between PA and colloidal nanocrystal is through oxygen and the low energy orbital level of oxygen may sink the passing electron during charge transfer or transport that lead to loss in photocurrent. Mercapto group could be a better choice, since S has much lower electronegativity and higher
orbital level and –SH can lose an electron to bind with colloidal nanocrystals (Chapter 7).

10.2.1.3 Organic-inorganic hybrids

The typical approach to prepare organic-inorganic hybrids is by directly blending organic semiconductors with colloidal nanocrystals in organic solvent mixtures. The solubility of organic semiconductors is typically given by alkyl side chain; while the dispersity of colloidal nanocrystals in organic solvents is provided by surface ligands. These surface ligands are typically insulating for charge transport and also able to serve as recombination / trapping centers for photogenerated excitons and charge carriers. An alternative approach to prepare organic-inorganic hybrids is by in-situ synthesis. For example, P3HT:CdS hybrids prepared by in-situ wet-chemistry method as the active layer leads to $\eta_p \sim 3\%$,\textsuperscript{156} low-gap polymer (PSiF):CuInS hybrid prepared by decomposing the CuInS precursors within the polymer matrix as active layer results in $\eta_p 2.8\%$,\textsuperscript{161} several times higher than those cells prepared by blending CuInS nanoparticles with conjugated polymers. Nonetheless, the challenge for this approach is to select appropriate precursors and solvents for colloidal nanocrystal growth at relatively low temperature. The solvents should not only have affinity with precursors, but also the organic semiconductors. So far, though there are very limited nanocrystals that can be grown within a polymer matrix at low temperature, it is still a promising approach to integrate hybrid materials preparation and device application.

10.2.2 Multi-junction Organic-inorganic Hybrid PV Cells

Stacking cells in series is another approach to improve the efficiency of hybrid solar cells. The photogeneration can be maximized by readily designing the optical distribution in each subcell and concurrently the photovoltage of each subcell can be
added. The tandem all-organic solar cells have shown some success recently, while there is still no literature report of solution-processed tandem hybrid solar cells, partly because the device fabrication is much more complicate than single-junction cell.

Figure 10-2 shows a tandem cell composed of a front solution-processed hybrid subcell, a back vacuum-deposited small-molecule subcell, and ZnO/PEDOT:PSS/MoOx charge recombination zone (CRZ). The broad spectral response of PCPDTBT:CdSe cell could harvest near-infrared solar photon. Though the SubPc/C60 cell can only absorb the visible photon, it can produce large open-circuit voltage. The preliminary result shows $J_{sc}$ of the tandem cell close to the $J_{sc}$ of the current-limiting SubPc/C60 cell; and the $V_{oc}$ of the tandem cell is close to the addition of those of the two subcells, suggesting the efficient charge recombination at CRZ. High-efficiency tandem hybrid

Figure 10-2. (color) $J–V$ characteristics of a tandem cell containing a PCPDTBT:CdSe hybrid cell and a small-molecule cell using ZnO NPs as inter-connecting layer and the corresponding subcells.
solar cells are anticipated if the front and back subcells were optimized to balance photon-harvesting. In addition, by replacing SubPc/C60 with PBnDT:CdSe, all-solution-processed tandem hybrid solar cells with both large $V_{oc}$ and high efficiency are envisioned.
APPENDIX
LIST OF PUBLICATIONS AND CONFERENCE PRESENTATIONS

Publications


*Conference Presentations*


Annual Joint Symposium of the FLAVS and FSM, Invited talk for young leaders section, Orlando, Mar. 2012.


9. *(Invited)* Jiangeng Xue,* Renjia Zhou,* Lei Qian, Ying Zheng, Jihua Yang, Aiwei Tang, Paul H. Holloway, Hybrid Photovoltaic Cells based on Conjugated


LIST OF REFERENCES


146. Milliron, D. J.; Gur, I.; Alivisatos, A. P. MRS Bull. 2005, 30, 41-44.


BIOGRAPHICAL SKETCH

Renjia Zhou was born in Sanming, Fujian Province, China. He studied in Polymer Science and Engineering and obtained the Bachelor of Science from Zhejiang University at 2006. He continued the study at Zhejiang University and majored in Chemistry for a Master of Science from 2006 to 2008, and worked on chemistry of colloidal nanocrystals and carbon nanotubes with Prof. Hongzheng Chen and Prof. Mang Wang.

Then he moved to University of Florida to pursue a Doctor of Philosophy at Department of Materials Science and Engineering since 2008, where he has worked with Prof. Jiangeng Xue and focused on development of colloidal nanocrystals for optoelectronic devices, particularly organic-inorganic hybrid photovoltaic cells. He has published 20 peer-reviewed papers in the field of nanostructured materials and optoelectronic devices. He will head to the Molecular Foundry at Lawrence Berkeley National Laboratory to start a postdoctoral position.