INCORPORATING DOUBLE-HETEROJUNCTION IN ANISOTROPIC SEMICONDUCTOR NANOCRYSTALS FOR NOVEL OPTOELECTRONIC APPLICATIONS

BY

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DISSERTATION

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ABSTRACT

As semiconductor heterostructures play critical roles in today’s electronics and optoelectronics, the introduction of active heterojunctions can impart new and improved capabilities that will enable the use of solution processable colloidal quantum dots (QDs) in future devices. Such heterojunctions incorporated into colloidal nanorods may be especially promising since the inherent shape anisotropy can provide additional benefits of directionality and accessibility in band structure engineering and assembly. Here, we develop double heterojunction nanorods where two distinct semiconductor materials with type II staggered band offset are both in contact with one smaller band gap quantum dot. The double heterojunction can provide independent control over the electron and hole injection/extraction processes while maintaining high photoluminescence yields and shape anisotropy.

Developing new synthetic routes for the formation of ideal double heterostructures, we find that unexpected etching of nanocrystals by one of the most commonly used metal precursors, metal oleates. Especially, Zn-oleate is shown to etch CdS nanorods anisotropically, where the length decreases without a significant change in the diameter. Sodium oleate enhances the etch rate whereas oleic acid alone does not cause etching, indicating the importance of counter cation on the rate of oleate induced etching. Subsequent addition of Se precursors to the partially etched nanorod in Zn-oleate solution can lead to epitaxial growth of CdSe particles rather than the expected ZnSe growth despite an excess amount of Zn precursors being present. The composition of this epitaxial growth can be varied from CdSe to ZnSe depending on the amount of excess oleic acid or the reaction temperature. Similar tuning of composition can be observed when starting with collinear CdSe/CdS/CdSe rod/rod/rod heterostructures and spherical CdS (or CdSe/CdS core/shell) nanocrystals. Conversion of collinear rod/rod/rod structures to barbells and interesting rod growth from nearly spherical particles among other structures can also result due to the initial etching effect.
of metal oleates. These observations have important implications on our understanding of nanocrystal heterostructure synthesis and open up new routes to varying composition and morphology of these materials.

One of the most interesting applications of the semiconductor nanocrystals is display device applications such as LEDs incorporating QDs (QD-LEDs) as the electroluminescent layer. Recent advances in QD-LEDs have led to efficiencies and brightness that rival the best organic LEDs. Nearly ideal internal quantum efficiency being achieved leaves light outcoupling as the only remaining means to improve external quantum efficiency (EQE) but that might require radically different device design and reoptimization. However, the current state-of-the-art QD-LEDs are based on spherical core/shell QDs, and the effects of shape and optical anisotropy remain essentially unexplored. Here, we demonstrate solution-processed, red-emitting double-heterojunction nanorod (DHNR)-LEDs with efficient hole transport exhibiting low threshold voltage and high brightness (76 000 cd/m²) and efficiencies (external quantum efficiency (EQE) = 12%, current efficiency = 27.5 cd/A, and power efficiency = 34.6 lm/W). EQE exceeding the expected upper limit of ~8% (based on ~20% light outcoupling and solution photoluminescence quantum yield of ~40%) suggests shape anisotropy and directional band offsets designed into DHNRs play an important role in enhancing light outcoupling.

With increasing demand for complex, multifunctional electronics in light-weight and compact format, a dual ability to convert electricity into different forms of energy/signal including mechanical, thermal, and radiant and, conversely, to generate electrical energy/signal from these other forms is an attractive feature. However, developing such a two-way electronic device that performs both roles reasonably well may be difficult since improving performance of one function may lead to degradation of the other. Such a challenge can be seen in LEDs that also function as photodetectors (PDs). For example, donor-acceptor blends often used for efficient charge separation in organic photovoltaics or PDs usually quench photoluminescence and therefore are unlikely to perform satisfactorily as electroluminescent materials in OLEDs. Separate single-function devices (e.g., separate LEDs and PDs) can be integrated into systems that can perform reversible processes, but the design requires twice as many devices and a more
complex fabrication process. Here, we demonstrate highly efficient and fast light-responsive LEDs based on semiconductor nanocrystal quantum dots. In particular, anisotropic heterostructured nanorods are used as both light emitting and detecting materials. Band offsets designed into the nanorods can facilitate both charge recombination and separation and the anisotropic shape enhances light outcoupling and collection, ultimately allowing one device to function as both high performance LED and PD.

Despite of the multifunctionality and fascinating applications of double heterostructures in nanocrystal system, in case of cadmium-based II-VI semiconductors, the presence of toxic elements has rendered their practical usage unlikely or at best difficult. We also develop Cd-free luminescent DHNRs with I-III-VI compound semiconductors. Based on the same etching and re-growing effect investigated with Cd-based materials, Facilitating those metal oleate in I-III-VI₂ semiconductors enables to achieve the direct formation of heterostructures with CuInS₂ and CuInSe₂ on CuGaS₂ nanorods, which has not been reported yet anywhere to the best of our knowledge. Interesting sawtooth structures and branch structures has been analyzed with high resolution TEM, STEM and EDS. After growing ZnSe or ZnS shell on the CuGaS₂/CuInSe₂ NRHs distinct PL and other interesting/useful optical properties, including large Stokes shift, charge transfer between components, and long lived excitons, were observed.
To my parents and my family, for their love and support.
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CHAPTER 1

INTRODUCTION

Most interesting properties of today’s electronic and optoelectronic devices, including high electron mobility, light emission, lasing and photocatalytic effect arise from combinations of two or more different kinds of semiconductor materials. One can expect that combining dissimilar semiconductors brings about superior characteristics to inherent nature of the respective components by means of forming the interface where the additional functionality can emerge between the semiconductors. The development of semiconductor heterostructures has enabled tremendous progress in electronics and optoelectronics.

Nano-sized colloidal forms of semiconductor heterostructures that can be synthesized by versatile solution chemistry are currently being considered for advancing multiple areas of technology. In addition to the well-known size-dependent optical properties of semiconductor nanocrystals arising from the quantum confinement effect, heterostructured nanocrystals also have valuable interfaces between each component. The hetero-interfaces can lead to improved and/or new optical and electronic properties that depend on the energy band alignment. In particular, the formation of straddling band offset (type I) at the interface enables higher photoluminescence quantum yields than those of single component materials by effectively confining charge carriers. The effective carrier confinement and recombination show much promise in imaging, lighting and display applications. On the other hand, staggered band offset (type II) may be useful in directing charge carriers. The cascading type II structures have been shown to allow photoinduced charge separation and light amplification. Hence, heterojunctions in nanocrystals allow the benefits of manipulating charge carriers including confinement, extraction and injection of electrons and holes.

To date, the core/shell nanocrystals having type I heterojunction is the predominant choice in emerging nanocrystal-based products. The passivation of the shell stabilizes the core surface, and therefore can contribute to the luminescence enhancement. However, the core/shell structure may be less than ideal
especially in photovoltaics, optoelectronics and related device applications in that the large band gap shell prohibits physical access to the core and poses significant barrier for carrier injection and extraction\textsuperscript{10}. In order to exploit advantages of semiconductor heterojunctions in solution-synthesized nanocrystals, having at least two components physically accessible may be desirable (e.g., for charge injection and extraction). Recent advances in synthesis that allow multi-component colloidal semiconductor nanocrystals with complex anisotropic shapes/morphologies\textsuperscript{11} provide a potential solution. When combined with band alignment/band gap engineering of semiconductor heterostructures, anisotropic nanocrystals can provide control over both spatial and electronic directionality and accessibility. However, the applications of these anisotropic nano-materials have been rather limited because of the larger surface area which can cause more charge carriers to be trapped.

Based on the discussion of heterostructures above, controlling band alignment/offset via epitaxially well-defined heterostructures can be a ubiquitous solution for manipulating charge carriers. Of special note over the past few decades is the double-heterostructure where a narrower band gap semiconductor is placed between wider band gap materials\textsuperscript{12} (Figure 1.1). Charge carriers can effectively be confined in a light emitting region surrounded by two different heterojunctions. The quasi-electric potential barriers at each end of the active region can prevent the outflow of injected electrons and holes. It is also additional benefits of this structures to enable low threshold voltage and reduced heating, allowing increased output/performance before reaching thermal limitations\textsuperscript{13}. The double-heterostructure has enabled semiconductor lasers and is now widely used in LEDs and bipolar transistors among many devices\textsuperscript{12,14}.

**Figure 1.1.** Band diagram of the double-heterostructure laser, as originally published in Proceeding of the IEEE (Kroemer, 1963)\textsuperscript{12}.
1.1. Objective 1: Incorporating Double-Heterojunction in Nanocrystal System

Incorporating double-heterojunction in a nanorod (DHNР) that are analogous to epitaxial thin film double heterostructures requires the growth of two distinct larger band gap materials of type II band offset (or p- and n-doped materials) surrounding one semiconductor. In the thin film geometry, deposition on to a substrate allows symmetry breaking and the sequential growth inherently leads to the middle component being interfaced with two different materials. In the solution synthesis of nanocrystal heterostructures, such a growth becomes challenging because the “substrate” is a soluble particle that may often prefer surface area-reducing core/shell type structure and therefore means of growth that is spatially selective must be imposed for each added component.

To achieve our envisioned DHNRs, there are additional difficulties. For example, the two larger band gap materials (i.e., CdS and ZnSe) are likely to be better lattice matched with each other than with the smaller gap material (i.e., CdSe) leading to unwanted interfaces. Imposing growth only to be along the rod axis can lead to double heterojunctions in collinear structures but the smaller gap emitting materials will have partially exposed surfaces limiting desired characteristics such as high PL yields. Perhaps even more importantly, a diversity of the epitaxial heterojunction that can be formed on the surface of nanorods beyond heterojunctions at the tips can provide new morphologies with new means of controlling optical properties. These challenges associated with the heterostructure formation, thus far, have not been addressed using solution chemistry but the ability to epitaxially grow two distinct materials around a nanocrystal should in general lead to a whole new subclass of complex nanomaterials with multiple functionalities.

1.2. Objective 2: Fabrication of Highly Efficient Solution-Processable DHNR-LEDs

One of the main reasons for the less-than-ideal performance of conventional QD-LEDs is the large offset between HTL Fermi level and the valence band edge of QDs, leading to a large hole injection barrier. In addition, solubility of organic HTLs in solvents for QDs can cause damage or intermixing. Recent
introduction of the inverted structure, where ITO is the cathode and Al the anode with vacuum-deposited organic HTL and oxide HIL, has alleviated these problems, however, fabrication of QD-LEDs has become more cumbersome, requiring both solution and vacuum deposition. Hence, simple improvements that simultaneously enable solution deposition and the reduction of hole injection barrier are highly desirable. Furthermore, nearly ideal internal quantum efficiency being achieved leaves light outcoupling as the only remaining means to improve external quantum efficiency (EQE). Thus, it is important to understand and develop the methods to enhance light extraction.

1.3. Objective 3: Light-Responsive LEDs for Novel Display Applications

With increasing demand for complex, multifunctional electronics in light-weight and compact format, a dual ability to convert electricity into different forms of energy/signal including mechanical, thermal, and radiant and, conversely, to generate electrical energy/signal from these other forms is an attractive feature. However, developing such a two-way electronic device that performs both roles reasonably well may be difficult since improving performance of one function may lead to degradation of the other. Such a challenge can be seen in light emitting diodes (LEDs) that also function as photodetectors (PDs). For example, donor-acceptor blends often used for efficient charge separation in organic photovoltaics or PDs usually quench photoluminescence and therefore are unlikely to perform satisfactorily as electroluminescent materials in OLEDs. Separate single-function devices (e.g., separate LEDs and PDs) can be integrated into systems that can perform reversible processes, but the design requires twice as many devices and a more complex fabrication process. Thus, to understand and reveal such new capabilities of nanocrystals based on dual-functioning as a LED and a PD is important to develop futuristic display devices such as touchless interactive screens and self-powered display devices and extremely high speed display to display visible light communication.
1.4. Objective 4: Cd-Free DHNRs

There is a scarcity of anisotropic Cd-free nanocrystalline materials with comparable optical properties and the lack of depth in understanding of how geometry (along with surface chemistry) affects optical properties of these materials. Then, developing high-performance Cd-free anisotropic nanocrystals and their heterostructures is arguably the biggest missing part of the bridge between proof-of-concept and practical implementation of anisotropic nanocrystal heterostructures in next-generation technologies. The knowledge gained from achieving the above objectives and double-heterojunction nanorods with Cd based II-VI semiconductors can however provide design criteria/insights on developing useful morphologies of new Cd-free anisotropic nanocrystal heterostructures. The characterization, including atomic level high-resolution HAADF STEM imaging, directly translate to characterization of Cd-free materials to be developed. Better understanding of reaction/growth mechanisms help to identify and address critical issues such as etching/ripening of nanorods, growth of secondary components and composition variation in obtaining desired heterostructures.
CHAPTER 2

DOUBLE-HETEROJUNCTION NANORODS

Significant components of this chapter were published as “Double-Heterojunction Nanorods”, Nuri Oh, Sooji Nam, You Zhai, Kishori Deshpande, Pete Trefonas and Moonsub Shim, Nature Communications 5, 33642 (2014)\(^\text{15}\).

2.1. Introduction

Introducing structurally and electronically well-defined multiple heterojunctions within a nanocrystal can lead to the benefits in manipulating charge carriers, which has been described in the previous chapter, and facilitate utilization of unique characteristics of colloidal nanocrystals. First, we suggest the colloidal nanocrystal heterostructures which possess double-heterojunction and maintain the anisotropic shapes\(^\text{15}\). These double-heterojunction nanorods (DHNRs) exhibit high PL yields similar to type I core/shell structures since the emitting component is surrounded by larger band gap materials with type I band offset. The two distinct outer materials within the rod-based geometry can allow directionality and tuning of barriers for electrons and holes independently. This may especially be beneficial in light-emitting diode (LED) applications as described in chapter 4 and 5.

2.2. Synthesis and Characterization of DHNRs

Our approach to DHNRs combines the preferential growth along [001] direction of wurtzite semiconductor nanorods with core/shell-like growth. Figure 1a shows the band diagram and the schematic of DHNRs synthesized here where CdSe is interfaced with both CdS and ZnSe. CdSe, which forms type I band offset with both CdS and ZnSe, becomes the emitting/charge recombination center. CdS and ZnSe form type II band offset and can facilitate electron and hole injection, respectively. Their band alignment
should also make these two outer layer materials useful for blocking opposite charge carriers. The synthesis of DHNRs begins with CdS nanorods (Figure 2.1b and 2.1c) followed by selective growth of CdSe at the tips (Figure 2.1d and 2.1e) much like the barbell or rod/rod/rod shaped type II nanorod heterostructures of CdTe/CdSe/CdTe that have been reported previously\textsuperscript{16–18}. The key distinction and thus the main challenge here is the selective growth of the third component, ZnSe. By optimizing reaction temperature and time as well as the amount of ZnSe precursors, the desired selective growth of ZnSe on CdSe (Figures 2.1f and 2.1g) can be achieved while maintaining the tight size distribution of the initial CdS nanorods. Considering the lattice mismatch, which is the largest between CdSe and ZnSe (~7%), this selective growth may be surprising and therefore should be analyzed in further detail as we discuss below. Nevertheless, since the net change in the surface/interface energy rather than lattice strain alone dictates the overall energy of the system, we suspect that lower surface energy of the exposed CdS facets leads to this preferential growth on CdSe tips\textsuperscript{19–21}.  

**Figure 2.1. Double heterojunction nanorods (DHNRs).** (a) Energy band diagram and schematic of the geometric structure of DHNRs consisting of type II band offset CdS and ZnSe both in contact with the emitting smaller band gap CdSe quantum dot. (b)-(g) Representative TEM and STEM images of CdS nanorod seeds (b and c), CdS/CdSe nanorod heterostructures (d and e), and CdS/CdSe/ZnSe double heterojunction nanorods (f and g). Electron microscopy images show the shape evolution during each step of the formation of DHNRs. Scale bars are 50nm for b, d and f (insets: 5nm) and 100nm for c, e, and g (insets: 10nm).
Characterization of selective growth of ZnSe on CdSe is arguably as important as the optimum synthesis conditions and multiple independent techniques should be utilized to confirm the composition and structure. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images as exemplified in Figures 2.1f and 2.1g show that the rod/rod/rod shape of CdSe/CdS/CdSe changes to a more barbell-like structure upon ZnSe growth. This ripening of the tips is consistent with the expected selective growth on CdSe. The average diameter changes from 4.2 to 5.5 nm at the tips whereas it remains nearly constant at the center of the rods (change of ~ 0.5 nm or less). There is also an increase in the average overall length of ~3 nm, suggesting a growth of shell-like ZnSe over CdSe. Energy dispersive X-ray spectroscopy (EDS) results also show considerable amount of Zn (~12%) with an increased Se content verifying growth of ZnSe (Table 2.1). EDS analysis using aberration-corrected STEM to map composition at different regions of DHNRs shows that Zn and Se are concentrated at the tips and S at the center whereas Cd is uniformly spread throughout the DHNRs (Figure 2.2).

<table>
<thead>
<tr>
<th>EDS (%)</th>
<th>Cd</th>
<th>S</th>
<th>Se</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS nanorod seeds</td>
<td>54.4</td>
<td>45.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdS/CdSe heterostructures</td>
<td>54.6</td>
<td>37.5</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>DHNRs (0.10 mmol of Se)</td>
<td>43.5</td>
<td>30.5</td>
<td>14.0</td>
<td>12.0</td>
</tr>
<tr>
<td>DHNRs (0.25 mmol of Se)</td>
<td>38.7</td>
<td>25.1</td>
<td>19.2</td>
<td>17.0</td>
</tr>
<tr>
<td>DHNRs (0.50 mmol of Se)</td>
<td>30.8</td>
<td>18.4</td>
<td>25.1</td>
<td>25.7</td>
</tr>
</tbody>
</table>

**Table 2.1. Element analysis by EDS in TEM mode.** EDS analyses were carried out with over 100 nanorods to confirm the elemental composition change from CdS nanorods to CdS/CdSe nanorod heterostructures and CdS/CdSe/ZnSe double heterojunction nanorods. CdS nanorods and CdS/CdSe heterostructures showed slightly higher Cd contents due to Cd-rich synthesis condition. The increase of Se and Zn contents is consistent with ZnSe growth.
Powder X-ray diffraction (XRD) also shows evidence of selective ZnSe growth. The XRD patterns of DHNRs at each step of the synthesis are shown in Figure 2.3. Distinctive and sharp (002) peak of CdS does not change despite CdSe growth, indicating that CdSe grows along c-axis of CdS nanorods. As CdSe grows, additional peaks at smaller $2\theta$ values than the corresponding CdS peaks appear as expected of a larger lattice material of same crystal structure. The final step of ZnSe growth is difficult to detect with XRD given the average of ~2- to 3-monolayer-thickness expected from TEM and STEM images. The changes in XRD peak positions (from curve fitting in Figure 2.3) show an interesting result that supports selective growth of ZnSe. Peaks corresponding to CdS do not change appreciably but CdSe peaks are up-shifted significantly. The up-shifts correspond to a lattice constant decrease of ~0.1 % for CdS whereas CdSe exhibits an order of magnitude larger ~1.1 % decrease after ZnSe growth. What this result implies is that ZnSe growth places only CdSe under compressive strain due to the lattice mismatch. This decrease only in the CdSe lattice constant provides another important evidence for selective ZnSe growth.
Figure 2.3. X-ray diffraction patterns from each step of DHNR synthesis and calculated lattice parameters. The selective shifts in the CdSe peaks as analyzed by curve fitting shown indicate selective growth of ZnSe on CdSe necessary to achieve the desired double heterojunctions. Lattice parameters were averaged over the each peak position obtained from XRD patterns. Selective growth of ZnSe on CdSe causes reduction in both CdSe a- and c-lattice constants by 0.91 % and 1.31 %, while CdS lattice remains nearly constant.

To characterize composition distribution in the DHNRs with near atomic resolution, high-angle annular dark field (HAADF) imaging was carried out on an aberration-corrected STEM. Heavier elements have larger electron scattering cross-sections at high angles and thus higher intensity in the Z-contrast images. The atomic column resolution of Z-contrast afforded by the aberration-corrected STEM can therefore reveal composition variations within individual DHNRs allowing identification of heterointerfaces with near atomic precision. High-resolution HAADF STEM image in Figure 2.4a shows a tip of a DHNR consisting of CdS/CdSe barbell structure with a thin ZnSe layer (ZnSe thickness was controlled by the amount of Se added, 0.1 mmol in this case). The scattering intensity for each cation-anion column pair is always larger for the cation in the central part of the tip (Figure 2.4b, curve b1). This intensity difference is expected of CdSe since the cation is the heavier element. In contrast, there are several cases that exhibit higher scattering intensity for the anion when the outermost atomic columns of the tip are

<table>
<thead>
<tr>
<th>Average Lattice parameter (Å)</th>
<th>Before ZnSe growth</th>
<th>After ZnSe growth</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS part</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a axis</td>
<td>4.161</td>
<td>4.158</td>
<td>-0.07</td>
</tr>
<tr>
<td>c axis</td>
<td>6.718</td>
<td>6.710</td>
<td>-0.12</td>
</tr>
<tr>
<td>CdSe part</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a axis</td>
<td>4.305</td>
<td>4.266</td>
<td>-0.91</td>
</tr>
<tr>
<td>c axis</td>
<td>7.021</td>
<td>6.929</td>
<td>-1.31</td>
</tr>
</tbody>
</table>
analyzed (Figure 2.4b, curve b2). Figure 2.4c, curve c1 is a line scan of normalized cation-anion pair Z-contrast across the tip where the outermost pairs have higher anion scattering intensity. These Z-contrast inversions are expected in the presence of ZnSe since the cation is now the lighter element. Note that since each scattering peak corresponds to an entire column of atoms, we can expect a mixture of CdSe and ZnSe over the entire tip region but these outer regions would have larger contributions from ZnSe. Similar line scans of cation-anion pairs across the CdS region of the DHNR shows no obvious sign of ZnSe growth (Figure 2.4c, curve c2).

Figure 2.4. High-resolution aberration-corrected STEM analysis of ZnSe shell. (a) STEM image of CdS/CdSe/ZnSe DHNRs. Scale bar is 1nm. (b) Z-contrast intensity of representative individual cation-anion column pairs - labeled b1 (CdSe-rich center of the tip) and b2 (mixed CdSe and ZnSe outer region of the tip) in (a). (c) Z-contrast intensity analysis of cation and anion column pairs along the perpendicular direction to the rod axis. Filled circles correspond to the direction indicated for dotted rectangle labeled c1 in the STEM image of (a). Open squares correspond to the direction indicated for dotted rectangle labeled c2 in the STEM image of (a). Z-contrast is defined as $(I_{anion} - I_{cation})/I_{cation}$, where $I_j$ is the count of scattered electrons for ion column j.

The absorption and PL spectral changes at each step of the synthesis provide interesting insights into both optical properties and composition/structure of the DHNRs. The bottom-most spectra in Figure 2.5a correspond to the seed CdS nanorods. Both absorption and PL exhibit narrow linewidths indicative of a very narrow diameter distribution. In particular, band-edge emission peak near 470 nm has full-width-at-half-maximum (FWHM) of 16 nm (84 meV). The growth of the CdSe tips leads to a new absorption feature near 585 nm and the corresponding PL from CdSe band edge.
The double-peaked PL spectrum of CdS/CdSe nanorod heterostructures arises from a bimodal size distribution of CdSe presumably due to differentiation of growth rates on the two ends of the seed CdS nanorod\textsuperscript{22-24} (Figure 2.6). The radial dimensions of the growing CdSe tips are within about a monolayer length of the seed CdS nanorod diameter but the longitudinal dimension is what becomes bimodal. One of the tips has length along the rod axis that is smaller than the rod diameter leading to the shoulder in the PL spectrum near 560 nm. Photoluminescence excitation spectra measured at two different emission wavelengths corresponding to two different CdSe sizes exhibit same CdS contributions indicating that both are attached to CdS seed nanorods rather than isolated particles (Figure 2.6). The two different growth rates may be exploited to develop single tipped DHNRs. Interestingly, the bimodal size distribution of CdSe does not cause significant line broadening in the final DHNRs. After ZnSe growth, we have observed emission intensity to increase up to ~15 times while a narrow single emission peak emerges. FWHM of DHNRs as

![Figure 2.5](image)

**Figure 2.5. The evolution of optical properties and geometric shape with ZnSe thickness.** (a) From bottom to top, absorption and emission spectra of CdS nanorods, CdS/CdSe nanorod heterostructures, and CdS/CdSe/ZnSe DHNRs of two different ZnSe amounts. (b) and (c), STEM images of different thickness of ZnSe grown on CdS/CdSe nanorod heterostructures. Scale bars are 20nm for b and c.
narrow as 24 nm (80 meV) has been observed (for the case of shown in Figure 5a second spectrum from top, FWHM is ~29 nm or 96 meV). As a comparison, the best CdSe/CdS core/shell QDs of similar emission wavelength show 20 – 30 nm PL FWHM$^{25,26}$. The convergence of the two CdSe PL peaks may be a result of enhanced growth of ZnSe on the smaller CdSe tip which in turn would lead to a larger redshift than the PL of the larger CdSe tip upon ZnSe shell growth$^{27}$. The 15 fold increase in PL while maintaining narrow linewidth and the narrow size distribution of the seed CdS nanorod despite the two-step growth is highly promising for developing more complex heterostructures. The change of double peak to single peak in PL spectra upon ZnSe growth will further be discussed in next chapter.

Figure 2.5a shows that continued ZnSe growth by injecting additional Se precursor leads to a further improvement in PL (reaching up to 39% absolute PL quantum yield so far without any other optimization, for example, by choosing different surface capping molecules). In the core/shell nanocrystals, continued shell growth can lead to decreasing PL yields due to lattice strain buildup$^{10}$. Figures 2.1f, 2.1g,
2.5b, and 2.5c as well as additional STEM and EDS analyses in Figures 2.7 indicate that ZnSe initially grows selectively on CdSe tips but eventually grows on the sides of the CdS seed nanorods. The continued increase in PL yields may then be explained by the passivation of CdS surface traps by ZnSe. Since the linewidth and the wavelength of the PL do not change, we conclude that the appearance of type II emission across the CdS/ZnSe interface is negligible. Furthermore, this side growth is not continuous and therefore maintains physical access to CdS (Figure 2.7), which will be beneficial for carrier injection and extraction processes. This side growth will further be discussed later on (Chapter 3).

Figure 2.7. Analysis of DHNRs grown with excess ZnSe (0.5mmol of TOP:Se injected). (a)-(c) STEM images of DHNRs. (d) EDS elemental maps of a single DHNR. (e) Line scan of Z-contrast comparison of atomic columns in rectangular box in (b). The abrupt Z-contrast change indicates transition from CdS part to ZnSe. (f) Electron scattering intensity of individual atomic columns labeled in (c).
2.3. Summary

The DHNRs achieved here represent the beginning of a new subclass of nanocrystals that incorporate both type I and type II band offsets where the heterojunctions are active rather than passive insulators. Specifically shown here is the case of two distinct materials both in contact with one CdSe QD facilitating electron and hole injection (and blocking of opposite charge carriers) independently. This type of ability to engineer band structure/offsets via functional heterojunctions with spatial anisotropy in colloidal nanorods affords exciting prospects for utilizing solution-processable nanomaterials for high-performance devices. As we discuss later on, DHNRs with independently variable electron and hole injection barriers are excellent candidate materials for electroluminescent devices. Furthermore, fine-tuning of composition or morphology (e.g., transition from double tip growth to multiple dot growth on the surface) should lead broader applicability of DHNRs (e.g., in photodetectors and photovoltaics) as well as further improvement in device performance. In general, building on the strategy to extend anisotropic nanorod growth to incorporate the double heterojunction (while maintaining narrow size distribution) should pave the way for developing synthesis of multi-component, multi-functional nanoheterostructures.

2.4. Experimental Details

Synthesis of double heterojunction nanorods: The reactions were carried out in a standard Schlenk line under N₂ atmosphere. Technical grade trioctylphosphine oxide (TOPO) (90%), technical grade trioctylphosphine (TOP) (90%), technical grade octylamine (OA) (90%), technical grade octadecene (ODE) (90%), CdO (99.5%), Zn acetate (99.99%), S powder (99.998%), and Se powder (99.99%) were obtained from Sigma Aldrich. N-octadecylphosphonic acid (ODPA) was obtained from PCI Synthesis. ACS grade chloroform, and methanol were obtained from Fischer Scientific. All chemicals were used as received.
CdS nanorods: CdS nanorods were prepared in a manner similar to established methods. First, 2.0 g (5.2 mmol) of TOPO, 0.67 g (2.0 mmol) of ODPA and 0.13 g (2.0 mmol) of CdO in a 50 ml three-neck round-bottom flask were degassed at 150 °C for 30 min under vacuum, and then heated to 350 °C under stirring. As Cd-ODPA complex was formed at 350 °C, the brown solution in the flask became optically transparent and colorless typically after 1 h. The solution was then cooled and degassed at 150 °C for 10 min to remove by-products of complexation including O₂ and H₂O. After degassing, the solution was reheated to 350 °C under N₂ atmosphere. S precursor containing 16 mg (0.5 mmol) of S dissolved in 1.5 ml of TOP was swiftly injected into the flask with a syringe. Consequently, the reaction mixture was quenched to 330 °C where the CdS growth was carried out. After 15 min, the CdS nanorods growth was terminated by cooling to 250 °C where the CdSe growth on CdS nanorods was carried out. An aliquot of the CdS nanorods was taken, and cleaned by precipitation with methanol and butanol for characterization. The CdS/CdSe heterostructures were formed by adding Se precursor slowly to the same reaction flask, maintained under N₂ atmosphere as described below.

CdS/CdSe nanorod heterostructures (NRHs): The one pot synthesis of rod-rod-rod shaped NRHs were carried out in a similar manner to established method. Following the formation of CdS nanorods, Se precursors containing 20 mg (0.25 mmol) of Se dissolved in 1.0 ml of TOP was slowly injected at 250 °C at a rate of 4 ml/h via syringe pump (total injection time ~ 15 min). The reaction mixture was then allowed to stir for an additional 5 min at 250 °C before being rapidly cooled by an air jet. An aliquot of CdS/CdSe NRHs was taken and cleaned by precipitation with methanol and butanol for analysis. The final solution was dissolved in chloroform, and centrifuged at 2000 rpm. The precipitate was redissolved in chloroform, and then prepared as a solution for the next step. This solution of CdS/CdSe NRHs had an optical density of 0.75 (in a cuvette with 1 cm optical path length) at the CdS band edge absorption peak when diluted by factor of 10.

CdS/CdSe/ZnSe double heterojunction nanorods (DHNRS): CdS/CdSe/ZnSe DHNRs were synthesized by growing ZnSe onto CdS/CdSe NRHs. For Zn precursor, 6 ml of ODE, 2 ml of OA and 0.18
g (1.0 mmol) of Zn acetate were degassed at 150 °C for 30 min. The mixture was heated to 250 °C under N₂ atmosphere, and consequently Zn oleate was formed after 1 hour. 2 ml of previously prepared CdS/CdSe stock solution was injected into Zn oleate solution after cooling to 50 °C. Chloroform was allowed to evaporate for 30 min under vacuum at 70 °C. ZnSe growth was initiated by a slow injection of Se precursor containing 39 mg (0.50 mmol) of Se dissolved in 2.0 ml of TOP to the reaction mixture at 250 °C. Thickness of ZnSe on CdS/CdSe NRHs was controlled by the amount of Se injected. The ZnSe growth was terminated by removing heating mantle after injecting desired amount of Se precursor. Cleaning procedures were same as described for the CdS nanorods.

**Device fabrication:** DHNR LEDs were fabricated on ITO-coated glass substrates (sheet resistance of 15~25 Ω/□). The pre-patterned ITO substrates were cleaned with acetone and isopropanol, consecutively, and then treated with UV-ozone for 15 min. PEDOT:PSS (Clevios™ P VP AI 4083), the HIL was spin-coated onto the ITO at 4000 rpm and baked at 120 °C for 5 min in air and 180 °C for 15 min in an argon glove box. Then TFB (H.W. Sands Corp.) as HTL was spin-coated using m-xylene (0.5 mg/ml) at 3000 rpm, followed by baking at 180 °C for 30 min in an argon glove box. After washing twice with chloroform and methanol mixture (1:1 volume ratio), CdS/CdSe/ZnSe DHNRs were finally dispersed in chloroform solution (~30 mg/ml), and spin-cast on top of the TFB layer at 500 rpm for DHNRs, and then subsequently annealed at 180 °C for 30 min in a glove box. ZnO as ETL (~30 mg/ml in butanol) was spin-coated at 3,000 rpm and annealed at 100 °C for 30 min. ZnO nanoparticles were synthesized following the literature. A solution of potassium hydroxide (1.48 g) in methanol (65 ml) was added to zinc acetate dihydrate (2.95 g) in methanol (125 ml) solution and the reaction mixture was stirred at 60 °C for 2 h. The mixture was then cooled to room temperature and the precipitate was washed twice with methanol. After ZnO spin-casting, ~100 nm thick Al cathode was deposited by an electron-beam evaporator at a rate of 1 Å/s. Finally, the devices were encapsulated using a cover glass with epoxy (NOA 86) in a glove box.

**Characterization:** Transmission electron microscopy (TEM) samples were prepared on Cu grids with thin carbon film from a dilute solution of nanorods in chloroform. TEM analysis was carried out with
a JEOL 2100 TEM operating at 200 kV. Energy dispersive X-ray spectroscopy (EDS) and scanning
tunneling electron microscopy (STEM) analyses were carried out with a JEOL 2200 aberration-corrected
STEM/TEM operating at 200 kV. UV-vis absorption spectra were obtained with an Agilent 8453
photodiode array spectrometer. PL spectra were collected with a Horiba Jobin Yvon FluoroMax-3
fluorometer. The absolute PL quantum yield was obtained using a Quantamaster 40 spectrophotometer.
DHNRs dispersed in toluene were dispensed in a 4 mL rectangular quartz cuvette and inserted into a sample
holder, within a dark sample chamber. Emission spectrum was obtained using a fixed excitation wavelength
(450 nm) and the emission wavelength was scanned between 400 - 800 nm with a 0.5 nm step size and
integration time of 0.1 seconds.
CHAPTER 3
METAL OLEATE INDUCED ETCHING AND FORMATION OF DOUBLE HETEROSTRUCTURES

Significant components of this chapter will be submitted as “Metal Oleate Induced Etching and Growth of Semiconductor Nanocrystals, Nanorods and Their Heterostructures” by Nuri Oh and Moonsub Shim.

3.1. Introduction

Advances in chemical synthesis of semiconductor nanocrystals (NCs) have led to an exquisite control over size, size distribution and even shape of a variety of materials into colloidal format that provides versatility in processing. Metal complexes with long chain carboxylates, amines and phosphonates are some of the most commonly used precursors for the synthesis of a variety of NCs. Such metal precursors are also important to the growth of heterostructures that provide enhanced optical/electronic properties often necessary for a successful implementation of new or improved applications utilizing these materials. For example, type I straddling band offset core/shell structures allow high photoluminescence (PL) necessary for biomedical imaging and type II staggered band offset heterostructures provide efficient photoinduced charge separation useful for photocatalysis or photovoltaics. Synthetic approaches to achieve well-defined and controlled NC heterostructures usually require exposure of pre-synthesized NCs to metal complex precursors at elevated temperatures for an extended period of time. An extreme example is the SILAR method to grow thick CdS shell on CdSe NCs which would take more than five days at 240 °C for 19 CdS layers. Carboxylic acids and related coordinating molecules (often in conjunction with another reagent) are known to etch and digest metal oxides. In fact, such an approach is commonly used to make metal oxide powders soluble in organic solvents to be used for NC synthesis. Yet, very little attention has been given to such etching effects.
during the synthesis of semiconductor NCs, especially in growing heterostructures. Here, we show surprising anisotropic etching of CdS nanorods (NRs) and CdS/CdSe nanorod heterostructures (NRHs) by one of the most commonly used reagents, metal oleates. It is the presence of metal oleates rather than oleic acid that leads to this unexpected etching. Addition of a more reactive chalcogen source can lead to growth that uses the etched metal ions in solution and the morphology and the composition of the resulting heterostructures can be varied by the amount of excess oleic acid and the reaction temperature. We also demonstrate that similar etching and growth effects can be seen in spherical NCs, including core/shell structures, leading to an interesting growth of islands or NRs from spherical NCs without the need for surface capping molecules that facilitate rod/directional growth.

### 3.2. Unexpected Heterostructure Formation

While etching of various NCs induced or assisted by amines, various oxidants, or photochemical means as well as anisotropic etching by certain acids or bases have been observed, metal carboxylates used as actual cation sources for NC growth causing such an effect has not been reported. This etching effect may have been concealed because it is difficult to distinguish the subtle size change before and after the reaction in spherical NCs. We became aware of this etching when we attempted to grow ZnSe on CdS NRs. When CdS NRs, after several purification steps to remove any leftover Cd and S reagents, were added to Zn-oleate solution in octadecene (ODE), the subsequent injection of trioctylphosphine selenide (TOPSe) led to the growth of islands of CdSe rather than the anticipated ZnSe on the seed CdS NRs. Figure 3.1 shows transmission electron microscope (TEM) images and absorption/PL spectra of the CdS NRs before and after this etch/growth process. Injection of TOPSe into CdS NR/Zn-oleate solution leads to an absorption peak at ~580 nm and a PL maximum at ~590 nm expected of CdSe NC band edge transitions while strong CdS absorption peak at 450 nm remains. Much higher Z-contrast intensity in the scanning transmission electron microscopy (STEM) image and the larger lattice spacing measured in high-
resolution TEM image in Figures 3.1b and c, respectively, confirm that the epitaxially grown particles on
the sides and tips of CdS NRs do indeed correspond to CdSe rather than ZnSe (Zn is lighter than Cd and
ZnSe should have smaller lattice spacing than CdS). High-resolution aberration-corrected STEM images in

Figure 3.1. Shape evolution of CdS nanorods in Zn-oleate/ODE solution before and after TOPSe injection.
(a) TEM image of CdS nanorod seeds. (b) High resolution Z-contrast STEM image after injecting TOPSe. Brighter
spots shown at the tips and the dots on the sides of nanorods indicate heavier elements, corresponding to CdSe. (c)
Magnified TEM image of side growth of secondary component on CdS nanorods. Lattice parameter of secondary
component is larger than CdS nanorods and consistent with CdSe. (d) Schematic illustration of multiple CdSe
growth on CdS nanorods due to unexpected etching rather than initially intended ZnSe growth. (e) Absorption
and emission spectra of CdS nanorods before and after TOPSe injection.

Figure 3.2 further verify that the Z-contrast between cation and anion columns is consistent with CdSe
growth. Energy dispersive x-ray spectroscopy (EDS) analysis also indicates that there is little or no increase
in Zn content upon TOPSe addition compared to NRs exposed only to Zn-oleate solution (Table 3.1). Based
on these results, we conclude that particles of CdSe form on the sides and tips of CdS NRs without any additional Cd precursors and despite the excess amount of Zn precursors in the reaction mixture.

![Image](image.png)

**Figure 3.2. High-resolution aberration-corrected STEM images of CdS NRs with second phase growth.**

The image clearly shows that the secondary component epitaxially grows at the side of CdS NRs and has larger lattice constant than the center part. The anion columns in the secondary component has much higher Z-contrast intensity of than CdS part. In addition, the Z-contrast intensity of anion columns in the secondary component is lower than cation columns. This intensity difference indicates that the composition of secondary component is consistent with CdSe (Cd is heavier than Se, but Zn is lighter than Se).

In this unexpected growth of CdSe on CdS NRs during an attempt to grow ZnSe, the only significant source of Cd is the CdS NRs themselves, implying possible etching of CdS NRs. To examine this potential etching effect and, if it is indeed occurring, to identify the etchant, purified CdS NRs were first exposed to an ODE solution containing only oleic acid and examined at different times of heating. Figure 3.3a shows
a TEM image of CdS NRs exposed to oleic acid in ODE at 250 °C for 2 h. The corresponding TEM image of CdS NRs before this treatment is shown in Figure 3.1a. No obvious structural changes are observable. When the same treatment was carried out using Zn-oleate instead of oleic acid, a noticeable decrease in length without a significant change in diameter was seen as shown in Figure 3.3b. The use of Na-oleate caused an even more noticeable decrease in length with a slight increase in diameter indicating a much faster etching rate with possible partial regrowth or ripening from free Cd/S in solution (Figure 3.3c). For these three reaction conditions, the same initial CdS NR solution was purified and divided into three batches. Figure 3.3d compares the changes in length and diameter of CdS NRs with annealing time using these three different reagents, quantifying the qualitative TEM observations of Figures 3.3a, b, and c. The etching time 0 min in Figure 3.3d corresponds to the time when the CdS NR solution reaches 250 °C (heat up time of 10 min). Figure 3.3e compares the absorption and PL spectra before and after 30 min and 2 h exposure to oleic acid or metal oleate solution. As expected, no significant changes are seen in the absorption spectra of oleic acid and Zn-oleate treated CdS NRs since the diameter of the NRs is not significantly altered in both cases. Oleic acid does, however, appear to improve surface properties as suggested by the increase in the CdS NR band edge PL. Na-oleate treatment, on the other hand, causes significant redshift and broadening of the CdS NR absorption features consistent with increasing diameter and decreasing aspect ratio observed in the TEM images. These observations indicate that it is the oleate anion rather than oleic acid that causes the etching of the NRs and the strength of coordination to the counter cation dictates the reactivity and therefore the etch rate. We note that there is a very recent report of oleate etching of rare-earth doped fluoride NCs, further emphasizing the importance of this unexpected etching.

The above discussed etching effects are further verified by the products arising from the addition of TOPSe to CdS NRs that have been etched. When CdS NRs are treated with oleic acid, we do not observe a secondary component growth with Se precursor addition as expected since there is an insignificant amount of etched Cd. This observation also verifies that unreacted Cd precursors from the initial CdS NR synthesis have been sufficiently removed. Na- or Zn-oleate treated CdS NRs, on the other hand, exhibit a significant
growth of the second component upon Se precursor addition. Side and tip growth of CdSe dots results from Zn-oleate etching and added TOPSe as seen in Figure 3.1 and Figure 3.4 and as discussed above. In the case of Na-oleate etching, a significant amount of separate homogeneous nucleation of CdSe NCs occurs, presumably due to a relatively high concentration of reactive Cd in solution (Figure 3.5). The observed side

![Figure 3.3. Etching effects of metal oleates on CdS nanorods. TEM image of CdS nanorod seeds in (a) oleic acid, and (b) Zn- or (c) Na-oleate/ODE solution for 4 hours at 250 °C, respectively. (d) Average length and diameter changes in each solution. CdS nanorods in Na-oleate solution become much shorter and more ripened than in Zn-oleate solution. There is no significant change in oleic acid solution. (e) Absorption and emission spectra before and after etching in each solution at 250 °C for 30 m and 2 h, respectively.](image)
growth of CdSe on CdS NRs with nearly spherical shape and large contact angle in the Zn-oleate case is uncommon compared to the more expected growth along the rod axis (or shell growth) for NRHs. Hence metal oleate induced etching can play an important role not only in the synthesis of semiconductor NCs but also in the synthesis of their heterostructures, in particular, in altering the morphology and composition of the products.

Figure 3.4. TEM images of CdS NRs with second phase growth. The different magnification images from (a) to (d) clearly show that the secondary components epitaxially grow at the side of CdS NRs. (e) TEM diffraction pattern reveals single-phase wurtzite crystal structure with the strong (002) peak, which indicates that the secondary components have similar (002) orientation with CdS NRs.
Along with the unexpected etching effect of metal oleates, the presence of excess oleic acid (with metal oleates) and the reaction temperature can provide some control over the composition of resulting NRHs which can in turn alter the morphology. Although many reported syntheses of NCs vary in the ratio of oleic acid to metal salts used and therefore the amount of excess oleic acid present in the reaction mixture, little consideration has been given to how this varying amount of excess oleic acid affects the growth of NCs or their heterostructures. Yet, whether or not excess oleic acid is present can alter products profoundly. For example, CdS shell can be grown on CdSe NCs using Cd-oleate if there is an excess amount of oleic acid but the same growth conditions without excess oleic acid has been shown to lead to separate nucleation of CdSe particles. Excess carboxyl acid has also been suggested to increase the solubility of metal precursors and thus suppress their reactivity. Similar effects of excess oleic acid can be seen in our system of CdS-based NRHs and can be exploited to alter the composition and morphology of the resulting NRHs. Without excess oleic acid, separate CdSe particles can nucleate upon TOPSe addition for the Na-oleate case where there is a large degree of etching and therefore high concentration of

Figure 3.5. Na-oleate etching effect on CdS NRs. (a) Low- and (b) high-resolution TEM images of CdS NRs after Na-oleate etching for 10 min and 0.1mmol of TOPSe addition. There is a significant amount of separate homogeneous nucleation of CdSe NCs occurs, presumably due to a relatively high concentration of reactive Cd in solution.

3.3. Controllable Shape and Composition of Heterostructures
Cd source in solution, similar to previous unsuccessful CdS shell growth attempt on CdSe NCs without excess oleic acid.\(^{71}\) When Zn-oleate is used where milder etching conditions lead to a lower concentration of Cd source in solution, CdSe particles of nearly spherical shape grow on both the tips and the sides of CdS NRs with large contact angles. This type of growth was observed when using Zn-oleate prepared by 1:2 or 1:4 molar ratio of Zn-acetate:oleic acid with no additional oleic acid added to the reaction mixture. On the other hand, Figure 3.6 shows that, after etching of CdS NRs with Zn-oleate prepared with excess oleic acid (1:12 molar ratio of Zn-acetate:oleic acid), the addition of TOPSe leads to tip and side growth of particles that have smaller lattice spacing and with significantly smaller contact angles. The smaller lattice spacing, smaller contact angle, and hence larger interface areas with CdS may be explained by the formation of CdZnSe alloy particles which would better match the CdS lattice than CdSe would. The absorption and PL spectra are also distinct from CdSe growth in the absence of excess oleic acid. The distinct CdSe band edge absorption peak converts to an absorption tail in the red as the amount of excess oleic acid in the reaction mixture is increased (Figure 3.6a). The PL intensity normalized to absorption at the excitation wavelength decreases by about an order of magnitude and becomes broader in width with increasing oleic acid.

Figure 3.6. Effect of excess oleic acid along with metal oleates. (a) Absorption and emission spectra of NRHs arising from Zn-oleate etching of CdS NRs with different amount or excess oleic acid followed by TOPSe injection. (b) Low- and (c) high-magnification TEM images of the NRHs formed with 1:12 ratio of Zn-acetate and oleic acid in ODE solution. The center part of the NRHs shows the similar lattice spacing with (002) planes of wurtzite CdS, while the components grown at the side faces have the smaller lattice spacing than (002) planes of wurtzite CdSe.
acid amount. The full-width-at-half-maximum of PL peak increases from 26.5 nm (95 meV) to 41.5 nm (149 meV) from no excess oleic acid case to the largest amount of excess oleic acid examined here (bottom-most and top-most spectra of Figure 3.6a, respectively). The increased line width and the drastic decrease in intensity of PL for the largest oleic acid amount case are consistent with spectral features arising from type II band offset between CdS and ZnSe (or Zn-rich CdZnSe). EDS results also show that a significantly larger amount of Zn gets incorporated during the second component growth on CdS NRs with excess oleic acid (Table 4.2) than without (Table 4.1). This enhanced incorporation of Zn may be due to a better stabilization of etched Cd in solution by excess oleic acid, effectively reducing its reactivity and therefore Zn-oleate becomes competitive in reacting with added TOPSe.

Another approach to increasing Zn content during the second phase growth step is to increase the reaction temperature. After CdSe growth on CdS NRs via Zn-oleate etching without excess oleic acid, if the reaction temperature is increased to 300 °C, the initial near spherical CdSe particles on the sides and tips of CdS NRs become larger and change to triangular cross-section as shown in Figure 3.7. For comparison, the initial CdS NRs and after near spherical CdSe growth at 250 °C is shown in Figure 3.1. There is a significant decrease in the lattice constant of the particles grown on the sides of the NRs from Figure 3.7. Effect of reaction temperature on Zn content in the second phase growth. (a) Low- and (b) high-magnification TEM images of the NRHs annealed at 300 °C. The pyramidal shaped second phase growth has the smaller lattice spacing than (002) planes of wurtzite CdSe. (c) Absorption and emission spectra of the resulting NRHs after injecting TOPSe following by annealing at 300 °C for 2 m.
Table 3.1. EDS element analysis of CdS etching/growth by Zn-oleate without excess oleic acid. EDS analyses were carried out on the several positions in TEM specimens to confirm the elemental composition change of the CdS NRs before and after etching, growth and annealing. Zn content which was detected after CdS NRs were transferred into Zn-oleate solution, indicates the presence of thin layer of Zn-oleate. However, there is little or no increase in Zn content upon TOPSe addition compared to Se content, which indicates that CdSe particles were formed without any additional Cd precursors and despite of the presence of excess Zn precursors. Further annealing at 300 °C reveals a significant increase in Zn content, which indicates that ZnSe or Zn-rich ZnCdSe alloy grows on the preexisting CdSe particles.

<table>
<thead>
<tr>
<th>EDS analysis (%)</th>
<th>CdS seeds</th>
<th>CdS NRs in Zn-oleate</th>
<th>0.25mmol TOPSe 0.25mmol TOPSe at 250 °C</th>
<th>Annealing at 300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>55.1 ± 0.4</td>
<td>49.5 ± 0.3</td>
<td>43.2 ± 0.8</td>
<td>33.8 ± 0.7</td>
</tr>
<tr>
<td>S</td>
<td>44.9 ± 0.3</td>
<td>45.1 ± 0.2</td>
<td>30.5 ± 0.5</td>
<td>23.1 ± 0.6</td>
</tr>
<tr>
<td>Zn</td>
<td>N/A</td>
<td>5.4 ± 0.4</td>
<td>8.1 ± 0.4</td>
<td>24.7 ± 0.6</td>
</tr>
<tr>
<td>Se</td>
<td>N/A</td>
<td>N/A</td>
<td>18.2 ± 0.7</td>
<td>18.4 ± 1.1</td>
</tr>
</tbody>
</table>

Table 3.2. EDS element analysis of CdS etching/growth by Zn-oleate with excess oleic acid. EDS analyses were carried out on the several positions in TEM specimens to confirm the elemental composition change of the CdS NRs before and after etching, growth and annealing. There is a significant increase in both Zn and Se contents upon TOPSe addition compared to the results in Table S1. The results reveals that excess oleic acid enhanced Zn incorporation into the secondary component because it may stabilize etched Cd better in solution reduce its reactivity, and thus lead to reactive Zn-oleate.

<table>
<thead>
<tr>
<th>EDS analysis (%)</th>
<th>CdS seeds</th>
<th>CdS NRs in Zn-oleate and excess oleic acid</th>
<th>0.25mmol TOPSe at 250 °C</th>
<th>Annealing at 300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>55.1 ± 0.4</td>
<td>45.9 ± 0.6</td>
<td>26.9 ± 0.6</td>
<td>14.8 ± 0.3</td>
</tr>
<tr>
<td>S</td>
<td>44.9 ± 0.3</td>
<td>44.9 ± 0.6</td>
<td>18.8 ± 0.3</td>
<td>10.9 ± 0.6</td>
</tr>
<tr>
<td>Zn</td>
<td>N/A</td>
<td>9.5 ± 1.0</td>
<td>29.9 ± 0.4</td>
<td>36.9 ± 0.9</td>
</tr>
<tr>
<td>Se</td>
<td>N/A</td>
<td>N/A</td>
<td>28.4 ± 1.1</td>
<td>37.4 ± 0.5</td>
</tr>
</tbody>
</table>
0.353 nm of CdSe at 250 °C (Figure 3.1c) to 0.340 nm after growth at 300 °C (Figure 3.7b). UV/Vis spectrum in Figure 3.7c shows slight red-shift of the band edge absorption near 580 nm as well as an increasing UV absorption. The PL efficiency increases significantly (~30% maximum PL efficiency observed) without much increase in the linewidth. These observations combined with EDS results in Table 3.1 showing a significant increase in Zn content only after annealing at 300 °C are consistent with CdSe growth at 250 °C being maintained (or slightly increasing in size) along with ZnSe or Zn-rich CdZnSe alloy overgrowth upon heating to 300 °C. Hence the reaction temperature and the amount of excess oleic acid present are critical parameters that can dictate whether type II staggered band offset (e.g., CdS/ZnSe) or type I straddling band offset (e.g., CdS/CdSe) heterostructures are obtained.

![Figure 3.8](image)

**Figure 3.8. Effect of Zn-oleate etching on CdSe/CdS/CdSe rod-rod shaped NRHs.** TEM images of (a) CdSe/CdS/CdSe seeds, after etching by (b) Na-oleate, (c) Zn-oleate and (d) oleic acid for 3 h at 250 °C. (e) Length and tip/center diameter changes in different oleate/ODE solution.

With a better understanding of how metal oleates alter the structure of CdS NRs and the subsequent heterostructure formation step, we now discuss how other CdS-containing NC/NR heterostructures are affected by this etching effect. Figure 3.8 summarizes the key results of oleic acid, Zn-oleate and Na-oleate
treatments of pre-synthesized and cleaned CdSe/CdS/CdSe collinear rod/rod/rod NRHs (referred to as CdS/CdSe NRHs from here on). Similar to CdS NR case, no significant changes are observed with oleic acid and decreasing length without a significant change in diameter (at the center of the NRs) are seen for Zn- and Na-oleate cases. The corresponding absorption and PL spectral changes are shown in Supporting Information Figure 3.9. The key difference is the ripening at the tips for the Zn- and Na-oleate cases leading

Figure 3.9. Absorption and emission spectra of CdS/CdSe NRHs before and after etching in each solution at 250 °C for 10 min, 60 min and 180 min, respectively.
to barbell-like structures with Zn-oleate leading to more uniform tips. High-resolution TEM images in the insets of Figures 3.8c and 3.8d indicate that the ripened tips have lattice spacing consistent with CdSe suggesting that it is mainly CdSe that gets etched and the higher reactivity of Se with Cd leads to re-growth or ripening. The addition of TOPSe to these CdS/CdSe NRHs etched/ripened by Zn-oleate leads to similar

![Figure 3.10](image)

**Figure 3.10. Effect of excess oleic acid on CdSe/CdS/CdSe NRHs with TOPSe injection.** TEM images of (a) the resulting NRHs after etching by Zn-oleate without excess oleic acid followed by injecting TOPSe and (b) the resulting NRHs with excess oleic acid.

![Figure 3.11](image)

**Figure 3.11. Absorption and emission spectra of CdS/CdSe NRHs** before and after etching by Zn-oleate at 250 °C for 2 hours and after injecting TOPSe.

32
growth as seen in the CdS NR case as shown in Figure 3.10. That is, without excess oleic acid, more CdSe-like particles with circular cross-section grow on the tips and sides of the initial NRHs whereas Zn-rich CdZnSe alloy particles with triangular cross-section appear with excess oleic acid.

Figure 3.12. TEM images of DHNRs which have the ideally grown ZnSe shell. The TEM images reveals that ZnSe growth are minimized at the sides of CdS NRs and maximized at the in CdSe tips. The DHNRs can be made by low-temperature TOPSe addition and fast-heating to 300 °C, retarding Zn-oleate etching and simultaneously inducing ZnSe growth.

It is interesting to note that CdS/CdSe NRHs originally exhibited two peaks in the PL, which begin to converge into a single peak upon this etching/ripening process (Figure 3.11). We had previously shown
that the two-peak PL arises from different size of CdSe at the tips from the initial single-pot synthesis of CdS/CdSe NRHs. Upon etching/ripening due to Zn-oleate, the asymmetric CdSe tips become similar in size eventually leading to a single-peak PL. This ripening effect is also responsible for the change from a double-peak PL of CdS/CdSe NRHs to a single-peak PL upon ZnSe growth to form CdS/CdSe/ZnSe double heterojunction NRs (DHNRs). We also note that the addition of TOPSe to CdS/CdSe NRHs in Zn-oleate solution under the same conditions as in Figure 3.10b leads to a large degree of side growth (of mainly CdSe in the case of no excess oleic acid – Figure 3.8c) whereas TOPSe injection in the DHNR synthesis leads to mainly ZnSe shell growth on CdSe tips. The key differences between these two syntheses are the temperature at which TOPSe is added and how the reaction temperature is changed after the addition. In the case of NRHs of Figures 3.8c and 4.10a, TOPSe is added at 250 °C after significant etching/ripening of the CdSe tips and allowed to react/grow at 250 °C. In the case of DHNRs, TOPSe is added at a lower temperature (i.e., 150 °C) where etching/ripening due to Zn-oleate has not yet initiated and the reaction temperature is ramped up to 300 °C rapidly, favoring ZnSe growth as expected from the results of increased reaction temperature discussed above (Figure 3.12).

Figure 3.13. Effect of Zn-oleate etching on CdSe/CdS core/shell NCs. TEM images of (a) CdSe/CdS core/shell seeds, (b) after etching with Zn-oleate without excess oleic acid and (c) after injecting TOPSe into the solution of (b) at 250 °C. (d) Resulting NCs from the same seeds of (a) after Zn-oleate etching with excess oleic acid followed by injecting TOPSe at 250 °C.
The Zn-oleate induced etching effects are also evident in CdSe/CdS core/shell NC heterostructures upon addition of TOPSe. Although there may appear to be some faceting, when CdSe/CdS core/shell NCs are exposed to Zn-oleate solution in ODE at 250 °C, the etching effects are not obvious in TEM images (Figures 3.13a and b). However, when TOPSe is added to the reaction mixture, surprisingly, CdSe rods begin to grow from nearly spherical dots in many instances (Figure 3.13c). Here, there are no capping molecules such as alkylphosphonic acids that induce preferential growth along a certain crystallographic direction. While further studies are necessary to sort out the mechanism that seems to prefer single rod
growth on each dot, partial exposure of CdSe due to etching or limited concentration of reactive Cd in solution may be contributing to such a selective growth. Similar irregular shell and rod (or dot) growths are also observed with and without excess oleic acid, respectively, when starting with CdS NCs rather than CdSe/CdS core/shell NCs (Supporting Information Figure 3.14 and 3.15). The addition of excess oleic acid with Zn-oleate leads to irregular shell growth (Supporting Information Figure 3.14c), consistent with what may be expected based on growth of ZnSe or Zn-rich CdZnSe alloy particles with triangular cross-sections observed in the CdS NRs and CdS/CdSe NRHs.

3.4. Summary

We have shown that CdSe rather than intended ZnSe can grow on CdS NRs and NCs in Zn-oleate solution despite the absence of intentionally added Cd precursors and excess amount of Zn precursors. This surprising result arises from anisotropic etching of CdS by Zn-oleate that leads to reactive Cd ions in solution. The degree of etching or the etch rate appears to depend on the strength of oleate coordination to its counter cation. The composition and the morphology of the second phase epitaxially grown on CdS NRs upon TOPSe addition after Zn-oleate induced etching can be varied either by the amount of excess oleic acid present or by the reaction temperature. Excess oleic acid as well as higher temperature enhances Zn incorporation during the epitaxial growth leading to more ZnSe-like structures with triangular cross-sections on CdS NRs. We have also shown that these effects are present in CdS/CdSe NRHs and CdSe/CdS core/shell NCs. In the case of CdS/CdSe NRHs which start out with asymmetric CdSe tips, etching and ripening of the tips lead to nearly symmetric barbell structures. For spherical NCs, conditions that favor CdSe growth leads to rod growth on the seed NCs whereas conditions that favor ZnSe growth leads to patchy shells. These findings not only imply how metal oleate induced etching can completely alter composition of the products in the synthesis of NC and NR heterostructures but also may pave the path to novel heterostructures with complex shapes.
3.5. Experimental Details

Materials. Triocetylphosphine oxide (TOPO) (90%), triocetylphosphine (TOP) (90%), oleic acid (90%), oleylamine (OAm) (70%), octadecene (ODE) (90%), CdO (99.5%), CdCl$_2$, zinc acetate (99.99%), sulfur (99.998%), and selenium (99.99%) were obtained from Sigma Aldrich. Sodium oleate (Na-oleate) (>97%) was obtained from Tokyo Chemical Industry. N-octadecylphosphonic acid (ODPA) was obtained from PCI Synthesis. ACS grade chloroform and methanol were obtained from Fischer Scientific. All chemicals were used as received.

Synthesis of CdS nanorod seeds. CdS NRs were prepared in a manner similar to established methods.$^{15}$ First, 2.0 g of TOPO, 0.67 g of ODPA and 0.128 g of CdO in a 50 mL three-neck round-bottom flask were degassed at 150 °C for 30 min under vacuum and then heated to 370 °C under Ar. After Cd-ODPA complex was formed at 370 °C, 16 mg of S dissolved in 1.5 mL of TOP was swiftly added into the flask with a syringe. Consequently, the reaction mixture was quenched to 330 °C where the CdS growth was carried out. After 15 min, CdS NR growth was terminated by cooling to room temperature. The final solution was dissolved in chloroform, centrifuged at 2000 rpm. The precipitate was re-dissolved in chloroform, and then prepared as a solution for the next step. This solution of CdS NRs had an optical density of 0.1 (for 1 cm optical path length) at the CdS band edge absorption peak when diluted by factor of 100.

Synthesis of CdS/CdSe NRH seeds. The synthesis of CdS/CdSe NRHs was carried out in a similar manner to an established method.$^{15}$ Following the formation of CdS NRs and cooling the reaction mixture from 330 °C to 250 °C, 20 mg of Se dissolved in 1.0 mL of TOP was slowly added at 250 °C at a rate of 4 ml/h via syringe pump (total injection time ~ 15 min). The reaction mixture was then allowed to stir for an additional 5 min at 250 °C before being rapidly cooled to room temperature. The final solution was dissolved in chloroform, and centrifuged at 2000 rpm. The precipitate was re-dissolved in chloroform, and then prepared as a solution for the next step. This solution of CdS/CdSe NRHs had an optical density of 0.1 (for 1 cm optical path length) at the CdS band edge absorption peak when diluted by factor of 100.
Synthesis of spherical CdS. The synthesis of wurtzite CdS nanocrystals was carried out in a similar manner to an established method. First, 0.046 mg of CdCl₂, 0.79 mL of oleic acid and 10 mL of di-n-octylether in a 50 mL three-neck round-bottom flask were heated to 250 °C under Ar atmosphere. 8 mg of sulfur dissolved in 0.825 mL of oleylamine (2.5 mmol) was swiftly injected to the flask with a syringe. After 10 min, the growth was terminated by cooling to room temperature. The resulting CdS NCs were purified by precipitation using a solvent mixture of chloroform and methanol followed by centrifugation. The supernatant was discarded and the precipitate was re-dispersed in chloroform for the next step.

Synthesis of spherical CdSe/CdS nanocrystal. The synthesis of wurtzite CdSe core was carried out in a similar manner to an established method. First, 0.060 g of CdO, 0.28 g of ODPA and 3 g TOPO in a 50 mL flask were degassed at 150 °C for 30 min under vacuum and then heated to 370 °C under Ar atmosphere. At this point, 1.5 g of TOP was injected into the flask. After the temperature recovered to 370 °C, 0.06 g of Se dissolved in 0.5 mL of TOP was swiftly injected into the flask. After 30 sec, the growth was terminated by cooling the reaction mixture to room temperature. The resulting CdSe seeds were purified by precipitation using a solvent mixture of chloroform, methanol and butanol and re-dispersed in chloroform. The synthesis of CdS shell growth was carried out in a similar manner to an established method. The Cd precursor for CdS growth was prepared by heating a mixture of 0.128 g of CdO and 3.16 mL of oleic acid in 10 mL of ODE to 250 °C. After cooling to room temperature, 0.21 mL of octanethiol was added to Cd-oleate/ODE solution and the solution was stirred for 30 min until the solution turned clear. For the CdS shell growth, 3 mL of ODE, 3 mL of oleic acid and 200 nmol of previously prepared CdSe seeds in a 50 mL flask were degassed at 150 °C for 30 min under vacuum and then heated to 310 °C under Ar atmosphere. During heating, the mixture of Cd and S precursors was slowly injected at a rate of 3 mL/hr starting at 240 °C. Once the injection was finished, 1 mL of oleic acid was swiftly injected into the flask at 310 °C. After 1 hr, the growth was terminated by cooling to room temperature. The resulting CdSe/CdS core/shell NCs were purified by precipitation using a solvent mixture of chloroform and methanol followed...
by centrifugation. The supernatant was discarded and the precipitate was re-dispersed in chloroform for the next step.

**Etching and regrowth with metal oleates.** A mixture of 0.184 g of Zn-acetate and various amount of oleic acid (from 0.64 mL to 3.82 mL) in ODE as indicated were prepared in a 50 mL three-neck round-bottom flask and degassed at 120 °C for 30 min under vacuum. Total volume of the reaction was maintained at 6 mL by adjusting the volume of ODE. The solution was then heated to 250 °C to form Zn-oleate. After 1 hour, the Zn-oleate solution was cooled to 60 °C. A purified solution of CdS NRs, CdS NCs, CdS/CdSe NRHs or CdSe/CdS core/shell NCs was injected into the solution and chloroform was allowed to evaporate for 30 min under vacuum. After heating to 250 °C, etching was carried out at this temperature for the duration as indicated. For experiments examining growth using etched Cd in solution, TOPSe solution containing 20 mg of Se in 1.0 mL of TOP was slowly injected at 250 °C at a rate of 4 mL/hr and the reaction mixture was allowed to stir at 250 °C for 5 min prior to cooling to room temperature. For high temperature annealing, the solution was heated to 300 °C after TOPSe injection and the reaction temperature was maintained at 300 °C for 5 min before being cooled down to room temperature. For Na-oleate etching, the procedure was the same as the Zn-oleate case except 0.304g of Na-oleate was used instead of Zn-acetate and oleic acid. For the control experiment to test the effect of OA, the same procedure was used except that only 1.13 mL of oleic acid was added without Zn-acetate or Na-oleate.

**Characterization.** TEM samples were prepared on Au grids with thin carbon film from a dilute solution of NCs in chloroform. TEM analysis was carried out with a JEOL 2100 TEM operating at 200 kV. EDS and STEM analyses were carried out with a JEOL JEM-2200FS aberration-corrected STEM/TEM operating at 200 kV. UV-vis absorption spectra were obtained with an Agilent 8453 photodiode array spectrometer. PL spectra were collected with a Horiba Jobin Yvon FluoroMax-3 spectrofluorometer.
CHAPTER 4

HIGH EFFICIENCY AND OPTICAL ANISOTROPY IN DOUBLE-HETEROJUNCTION NANOROD LIGHT-EMITTING DIODES


4.1. Introduction

Advances in QD-LEDs have led to efficiencies and brightness comparable to and driving voltage lower than those of organic LEDs (OLEDs), reaching an apparent limit on internal quantum efficiency (IQE). Building on achievements in OLEDs, device architectures involving an organic hole transport layer (HTL), core/shell (C/S) QD emitters, and an oxide electron transport layer (ETL) have led to the best performing QD-LEDs thus far. One of the most promising architectures is the organic hole injection layer (HIL), organic HTL, C/S QDs, and oxide ETL all spin-cast sequentially on indium tin oxide (ITO) with a final Al cathode as we also demonstrated in the previous chapter. This design, which we refer to as the “conventional” device structure, allows convenient and scalable all-solution processing. However, efficiencies of these QD-LEDs have remained modest with maximum EQE < 2%. One of the main reasons for the less-than-ideal performance is the large offset between HTL Fermi level and the valence band edge of QDs, leading to a large hole injection barrier (HIB). Furthermore, solubility of organic HTLs in solvents for QDs can cause damage or intermixing. Recent introduction of the inverted structure, where ITO is the cathode and Al the anode with vacuum-deposited organic HTL and oxide HIL, has alleviated these problems, rendering efficiencies and brightness of QD-LEDs comparable to those of the best phosphorescent OLEDs while achieving smaller bandwidth and driving voltage. However, fabrication
of QD-LEDs has become more cumbersome. More importantly, nearly ideal IQE being reached leaves no obvious room for improvement other than drastically altering device design for better light outcoupling then re-optimizing to achieve high IQEs. Hence, simple improvements that simultaneously enable solution deposition and enhanced light extraction are highly desirables.

Heterostructures based on semiconductor nanorods are an emerging class of materials that represent a relatively unexplored domain especially with respect to LED applications. Optical anisotropy of nanorod heterostructures may provide additional benefits such as polarized light emission. However, non-C/S QD-based LEDs have suffered from poor efficiencies and there have only been a limited number of studies. Here, we examine the DHNRs as the light emitting layer in LEDs with “conventional” and inorganic-organic hybrid device structures. These devices exhibit narrow EL bandwidths, low threshold voltages, and stability under air operation with efficiencies comparable to the current state-of-the-art C/S LEDs using similar device structures. Given the recent finding of charging of CQDs from electron transport layer reducing device efficiencies (e.g., via multi-carrier Auger recombination), DHNRs with independently variable electron and hole injection barriers are excellent candidate materials for compensating or minimizing such loss mechanisms. More importantly, we demonstrate a simple means to even improve LED performance in conjunction with enhanced hole injection via the introduction of a hole dopant to the transport layer within a conventional solution processed device structure. Consideration of optical anisotropy in improving device characteristics suggests a fundamentally different and higher efficiency limit to these DHNR-LEDs.

4.2. Proof-of-Concept LED Devices Incorporating DHNRs

As we demonstrated that the established double-heterojunction structure allows high PL quantum yields with narrow linewidths in the Chapter 2, we now discuss the impact of the staggered band offset of CdS and ZnSe by examining the EL performance of DHNRs. First, LEDs with DHNRs as the emitting
elements (DHNR LEDs) were fabricated with device design similar to the “conventional” core/shell nanocrystal LEDs (C/S LEDs)\textsuperscript{6,87,88}. Figure 4.1a inset shows the schematic of our device structure. A cross-sectional TEM image is shown in Figure 4.2a. The device consists of a pre-patterned ITO anode and poly(ethylenedioxythiophene):poly(styrenesulphonate) (PEDOT:PSS) as the hole injection layer (HIL), poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,40-(N-(4-sec-butylphenyl)) diphenylamine)] (TFB) as the hole transport layer (HTL), DHNRs as the emissive layer, ZnO as the electron transport layer (ETL) and an electron-beam evaporated Al layer as the cathode. The DNHR emissive layer is approximately ~25 nm thick, which is less than the average length of the nanorods. This thickness and the SEM images of the DHNR film (Figure 4.2b) suggest that DHNRs are primarily orientated parallel to the device plane. The transport layers and electrodes have been used in C/S LEDs with EQE reaching up to ~1.7% for emission

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Device structure, energy band diagram, electroluminescence and device characteristics of the DHNR LEDs. (a) Energy band diagram of the DHNR LED along with schematic of device structure and a photograph of a working device. (b) EL spectra of a DHNR LED at the indicated applied current densities plotted along with the normalized PL spectrum of the DHNR film. (c) EQE vs. current density. Inset shows the dependence of luminance ($L$) on the applied voltage. (d) Dependence of current and power efficiencies on $L$.}
\end{figure}
wavelength comparable to our DHNR LEDs\textsuperscript{6,8,7,88}. Figure 4.1a shows the energy band diagram of our DHNR LEDs which should lead to efficient carrier injection to the DHNRs (especially for holes) due to the presence of the double heterojunction. Figure 4.1b shows the PL spectrum of our DHNR in film (dashed line) and EL spectra of the corresponding DHNR LED at the indicated current densities. Slight red shift of EL spectra compared with the PL spectrum can be seen with increasing current densities, which is expected based on the well-known Stark effect\textsuperscript{89}. The DHNR LEDs exhibit even narrower EL peak width (FWHM 29 nm, 96 meV) than previous C/S LEDs (38–39 nm, 115–131 meV) for EL peak position 600–640 nm\textsuperscript{6,77}. Furthermore, no parasitic emission from the adjacent layers (\emph{i.e.} TFB or ZnO) is observed over the entire device operation range (see Figure 4.1b).

![Image](image.png)

\textbf{Figure 4.2. Cross-sectional TEM images of DHNR LED, and SEM image of DHNR film.} (a) Cross-sectional TEM images of DHNR LED, consisting of a pre-patterned ITO anode and poly(ethylenedioxythiophene): poly(styrenesulphonate) (PEDOT:PSS) as the hole injection layer (~40 nm), poly[(9,9-diocetylfluorenyl-2,7-diyl)-co-(4,40-(N-(4-sec-butylphenyl)) diphenylamine)] (TFB) as the hole transport layer (~10 nm), DHNRs as the emissive layer (~25 nm), ZnO as the electron transport layer (~20 nm) and an electron-beam evaporated aluminum (~ 90 nm) layer as the cathode. (b) SEM image of DHNR film. Most DHNRs are placed parallel to the substrate.

Compared to the previously reported C/S LEDs using a similar device architecture, our devices exhibit lower threshold voltage (~1.3 V if defined as the point of the steep rise at the beginning of trap-limited conduction regime or ~1.6 V if defined as the driving voltage corresponding to a luminance of 0.1 cd/m\textsuperscript{2})\textsuperscript{5,6,87,90}. The maximum luminance of the DHNR LED shown in Figure 4.1c inset is 9,046 cd/m\textsuperscript{2}. The maximum EQE of DHNR LEDs measured thus far is 1.07 % (Figure 4.1c) and the corresponding maximum
current and power efficiencies are 2.23 cd/A and 2.27 lm/W, respectively (Figure 4.1d). These values are comparable to the best reported C/S LEDs using similar device architecture and emission wavelength and superior to the only other “nonspherical” nanocrystal based LEDs recently reported. Given that our devices simply “borrow” carrier injection and transport layers established for core/shell nanocrystals without any significant materials or thickness optimization for the new emissive layer (e.g., thickness and orientation of nanorod film, proper materials choice for the transport layers etc.), these achieved performances are noteworthy. More impressive are the low turn-on voltage, narrow EL bandwidth and the stability under air-ambient operation (Figure 4.3), which represent improvements over the best C/S LEDs with a similar device architecture reported to date. These promising characteristics of DHNR LEDs support our speculation that incorporation of double heterojunctions into the emitting nanocrystals can facilitate/enhance carrier injection processes.

<table>
<thead>
<tr>
<th></th>
<th>L (cd/m²)</th>
<th>Lifetime</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHNRs</td>
<td>1000</td>
<td>3.7 h</td>
<td>air</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>&gt; 3 d</td>
<td>air</td>
</tr>
<tr>
<td>Ref [115]</td>
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<td>~270 h</td>
<td>low vacuum</td>
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<tr>
<td>Ref [77]</td>
<td>500</td>
<td>~1 h</td>
<td>air</td>
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</tbody>
</table>

Figure 4.3. Luminance (L) change as a function of time measured under air-ambient condition and comparison of device stability of DHNR and C/S LEDs. DHNR LEDs exhibit excellent stability under air-ambient operation (~3.7 h half-life at initial luminance of 1000 cd/m² with a constant driving current density of 50 mA/cm²) and only ~4% decrease in luminance even after 70 h of continuous operation starting at 100 cd/m² with applying a constant driving current density of 15 mA/cm². Especially notable is the comparison to measurements in air of Ref. 77.
4.3. Reduced Hole Injection Barrier in DHNR-LEDs by F₄TCNQ

Despite of proper demonstration of DHNR-LEDs in the previous section, we have found that HIB due to the high HTL Fermi level and the solvent compatibility issue still remains significant. Once these shortcomings can be addressed, DHNRs may allow shape/optical anisotropy, directional type II band offset, and rod orientation to be exploited in enhancing device performance and enabling new capabilities. To solve the problems arisen from the current device structures and fabrication processes, we have introduced 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ), a well-known p-dopant for conjugated organics and related materials, to reduce HIB and improve IQE while maintaining convenient solution processing. Figure 4.4 shows the band diagram, chemical structures of the key components, device schematic and transmission electron microscopy (TEM) images of DHNRs and DHNR-LEDs. Scanning electron microscopy (SEM) of DHNRs spin-cast on poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,40-(N-(4-secbutylphenyl))diphenylamine)] (TFB)/F₄TCNQ HTL indicates that DHNRs are primarily oriented parallel to the device plane (Figure 4.4e). Naïvely, this orientation and the double-tipped nature of DHNRs may appear unfavorable - i.e., vertically-aligned single-tipped counterpart can have ZnSe and CdS

Figure 4.4. DHNR-LEDs (a) Energy band diagram of DHNR-LEDs. (b) Chemical structure of TFB and F₄TCNQ, and TEM image of DHNRs. (c) and (d) Schematic and cross-sectional TEM image of the DHNR LEDs. (e) SEM image of spin-cast DHNRs on TFB/F₄TCNQ HTL.
selectively contact their corresponding transport layers. However, as discussed later, parallel orientation of DHNRs can have a profound impact on light outcoupling.

Figure 4.5. Electronic and surface properties of TFB:F₄TCNQ film. (a) Secondary electron cutoff and highest occupied molecular orbital (HOMO) regions of the UPS spectra for HTL films with indicated TFB:F₄TCNQ weight ratios. Inset shows the Fermi level positions (dashed lines) and ionization potentials (IP) of TFB and TFB with F₄TCNQ along with valence band edges of ZnSe and CdS of DHNRs. (b) Thickness change of HTL with indicated TFB:F₄TCNQ weight ratios before and after chloroform exposure. (c)-(f) AFM and water contact angle (insets) images of TFB films with 1:0 (c), 1:0.1 (d), 1:0.4 (e), and 1:1 (f) TFB:F₄TCNQ weight ratio. The root mean square surface roughness of the pristine F₄TCNQ doped TFB films with 1:0, 1:0.1, 1:0.4, and 1:1 weight ratios are 0.26 nm, 0.32 nm, 0.38 nm, and 0.42 nm, respectively. The corresponding water contact angles are 101°, 101°, 102°, and 103°, respectively. Scale bars are 1 μm. We note that at 1:1 weight ratio, F₄TCNQ appears to have already reached solubility limit, which may explain the slightly larger change in thickness upon solvent exposure and larger surface roughness.
Ultraviolet photoelectron spectroscopy (UPS) indicates a monotonic increase in the ionization potential of HTL from 5.35 to 5.54 eV with increasing F₄TCNQ doping (Figure 4.5a), leading to a lowering of HIB (Figure 4.5a inset). Key energy levels with different amounts of F₄TCNQ are given in Table 3.1. The reduction in HIB up to 190 meV is in addition to that provided by the DHNR design (~400 meV by injecting holes through ZnSe rather than CdS). F₄TCNQ also improves HTL conductivity to better match ETL, which should help to balance charge in DHNRs (see Figure 4.6). Furthermore, F₄TCNQ significantly alters HTL solubility enabling solution processing. As shown in Figure 4.5b and Figure 4.7, the thickness of pristine TFB film is reduced considerably while F₄TCNQ doped TFB films exhibit a very small thickness.
change upon chloroform (solvent for DHNRs) exposure. Aromatic amine-containing polymers can be crosslinked by TCNQ upon electron transfer\textsuperscript{94} and we suspect that F\textsubscript{4}TCNQ causes both hole doping and ionic crosslinking of TFB. This crosslinking can then explain the improved solvent resistance of HTL. Interestingly, surface roughness and contact angle remain essentially unchanged upon F\textsubscript{4}TCNQ doping (Figures 4.7c-f), allowing for solution deposition without drastic changes to wetting behavior and DHNR orientation.

<table>
<thead>
<tr>
<th>TFB:F\textsubscript{4}TCNQ</th>
<th>Secondary cutoff (eV)</th>
<th>Fermi level (eV)</th>
<th>HOMO (eV)</th>
<th>Ionization potential (eV)</th>
<th>Energy barrier to ZnSe (eV)</th>
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<tr>
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<td>0.86</td>
</tr>
</tbody>
</table>

**Table 4.1.** Summary of Fermi level, highest occupied molecular orbital (HOMO) and the ionization potential of HTLs with respect to TFB:F\textsubscript{4}TCNQ weight ratio

### 4.4. Highly Efficient DHNR-LEDs

These advantages afforded by F\textsubscript{4}TCNQ along with the benefits of the double heterojunction designed into DHNRs lead to an exceptional LED performance. Very narrow (full width-at-half-maximum of 26 nm) and bright (76,000 cd m\textsuperscript{-2}) electroluminescence (EL) without parasitic emission from the transport layers is observed over the entire operation range with a threshold voltage (defined here as the voltage...
necessary to achieve 0.1 cd m\(^{-2}\) of only ~1.55 V (Figure 4.8). The threshold voltage being significantly lower than that of the band gap of the emitter (~2 eV) is currently under debate and may be associated with an Auger-related process\(^95\) or the presence of a charge prior to biasing due to charge transfer from the adjacent transport layers.\(^96\) While these characteristics are comparable to the best reported C/S QD-LEDs, current and power efficiencies of 27.5 cd A\(^{-1}\) and 34.6 lm W\(^{-1}\), respectively, exceed all QD-LEDs of similar emission wavelength (Table 3.2). The maximum EQE of our DHNR-LEDs is found to be 12.05 %. EQE vs. voltage plots for various TFB:F\(_{4}\)TCNQ ratios examined here are shown in Figure 4.9.

**Figure 4.8. Device characteristics.** (a) EL spectra of a DHNR-LED at the indicated applied voltages along with normalized solution PL spectrum of the DHNRs. Inset shows a comparison of solution PL with low bias EL. (b) Dependence of current and power efficiencies on luminance and a photograph comparing the brightness of C/S QD-LED and DHNR-LED both operating at 4 V (inset). (c) External quantum efficiency (EQE) vs. current density. Inset shows the dependence of luminance and current density on the applied voltage.
Figure 4.9. Characteristics of DHNR-LEDs with F\textsubscript{4}TCNQ. Current density-voltage-luminance curves (a) and EQE (b) vs. voltage plots of DHNR-LEDs for various TFB:F\textsubscript{4}TCNQ ratios.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>Emitting layer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>PL QY (%)</th>
<th>$V_{\text{on}}$ (V)</th>
<th>Max. $L$ (cd m$^{-2}$)</th>
<th>Peak EQE (%)</th>
<th>Peak CE (cd A$^{-1}$)</th>
<th>Peak PE (lm W$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>CdSe/ZnS core/shell</td>
<td>600</td>
<td>~80</td>
<td>1.7</td>
<td>31,000</td>
<td>1.7</td>
<td>3.9</td>
<td>3.8</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>CdSe/CdS/ZnS core/shell</td>
<td>618</td>
<td>&gt;70</td>
<td>&lt;2.0</td>
<td>~16,500</td>
<td>~1.6</td>
<td>~3.5</td>
<td>4.25</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>CdSe/CdZnS nanoplatelet</td>
<td>650</td>
<td>20~30</td>
<td>2~5</td>
<td>4,499</td>
<td>0.63</td>
<td>-</td>
<td>-</td>
<td>78</td>
</tr>
<tr>
<td>Inverted</td>
<td>CdSe/CdS core/shell</td>
<td>615</td>
<td>90</td>
<td>1.5</td>
<td>~50,000</td>
<td>18</td>
<td>19</td>
<td>25</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>CdSe/CdS/ZnS core/shell</td>
<td>630</td>
<td>70~80</td>
<td>1.8</td>
<td>23,000</td>
<td>7.8</td>
<td>5.7</td>
<td>-</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>CdSe/CdS/ZnS core/shell</td>
<td>630</td>
<td>70~80</td>
<td>1.8-2.0</td>
<td>57,350</td>
<td>-</td>
<td>5.78</td>
<td>7.12</td>
<td>82</td>
</tr>
</tbody>
</table>

Table 4.2. Comparison of the PL and EL characteristics of current-state-of-the-art of QD-LEDs with those of DHNR-LEDs.
4.5. Efficiency Comparison of DHNR-LEDs and C/S QD-LEDs

A comparison of the average EQE, current and power efficiencies, and brightness (Figure 4.10) with respect to F$_4$TCNQ doping for DHNR- and C/S QD-LEDs (both fabricated in the same manner in the conventional structure) demonstrate that our DHNR design is also critical to the exceptional performance of DHNR-LEDs rather than improvements afforded by F$_4$TCNQ alone. Efficiencies of DHNR-LEDs are routinely 2 to 3 times higher and brighter EL can be readily seen by the naked eye (Figure 4.8b inset). Note that EQEs between 2 and 6% of our control C/S QD-LEDs with F$_4$TCNQ already exceed the highest

Figure 4.10. Performance of QD- and DHNR-LEDs. Comparison of the average (a) EQE, (b) current efficiency, (c) power efficiency, and (d) peak luminance as a function of F$_4$TCNQ doping ratio for DHNR-LEDs and C/S QD-LEDs. Each data point is averaged over 4~6 devices per data point with the error bars representing the maximum and the minimum values for a given F$_4$TCNQ doping condition. The drop in all values at 1:1 TFB:F$_4$TCNQ ratio for both C/S QD and DHNR-LEDs likely arises from the solubility limit of F$_4$TCNQ.
reported values of ≤ 1.7% for red emitting QD-LEDs with conventional device structure. High efficiencies of DHNR-LEDs are especially impressive and surprising in that the solution PL QY of DHNRs is only about half that of C/S QDs. A comparison of PL spectra of DHNRs and C/S QDs used here (normalized to absorbance at the excitation wavelength of 400 nm) along with PL spectrum of a reference dye are shown in supplementary Figure 4.11 to verify that the DHNRs have same PL QY as Ref. 15 and that the PL QY of C/S QDs is about twice as large.

QD-LEDs that require relatively high operating voltages may have low efficiencies due to high field induced charge separation reducing PL QYs. High brightness at low voltages (e.g., >10,000 cd m⁻² already at 4V bias) and therefore low operating field should contribute to high efficiencies but the staggered band offset between CdS and ZnSe should make charge separation easier. The rod geometry placing CdSe emitters relatively far away from each other and therefore minimizing energy transfer loss (similar to thick ZnS shell QD-LEDs but without compromising turn-on voltage and power efficiency) is also likely to contribute to high efficiencies. A comparison of solution PL with low bias EL (Figure 4.8a inset) shows good overlap in peak position and linewidth supporting minimized energy transfer loss. However, these benefits alone cannot explain the 12% EQE which apparently exceeds the expected upper limit, suggesting that DHNRs provide yet additional benefits beyond improved carrier injection, low operating voltage and minimized energy transfer losses.

Figure 4.11. A comparison of PL spectra of DHNRs and C/S QDs used here (normalized to absorbance at the excitation wavelength of 400 nm) along with PL spectrum of a reference dye, 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-yran (DCM)
4.6. EQE Exceeding the Expected Limit: Anisotropy and Transition Dipole

In general, EQE is given by:

\[
EQE = (\gamma \times \eta_r \times q_{PL}) \times \eta_{out}
\]

The product in the parenthesis is the IQE and \(\eta_{out}\) is the light outcoupling efficiency.\(^{98}\) IQE is limited by the charge balance (\(\gamma\)), the radiative exciton production efficiency (\(\eta_r\)), and the PL QY of the emitter (\(q_{PL}\)).

Even if improvements due to F\(_4\)TCNQ and the additional reduction in HIB due to ZnSe of DHNRs allow us to reach ideal limits for \(\gamma\) and \(\eta_r\), \(q_{PL}=40\%\)\(^{15}\) and the assumption of maximum \(\eta_{out}=20\%\)\(^{99}\) limit the maximum EQE to 8\%, well below our measured 12\%. A histogram of EQEs with and without F\(_4\)TCNQ shown in supporting Figure 4.12 demonstrates that 77\% of the devices measured with optimum F\(_4\)TCNQ concentrations exhibit EQE > 8\%. We believe that the rod shape and the directional type II band offset increase \(\eta_{out}\) limit.

In OLEDs, several known factors reduce light output including loss to surface plasmons and waveguide modes.\(^{100}\) Such losses can be strongly dependent on the emitter dipole orientation.\(^{101,102}\) For a simple OLED structure, random dipole orientation leads to \(\eta_{out} \leq 20\%\) whereas surface parallel dipoles can theoretically lead to \(\eta_{out} > 40\%.\(^{103–105}\) Given that the majority of DHNRs lie flat on the substrate (e.g., SEM images of Figure 4.4e and Figure 4.13), we expect our DHNR-LEDs to fall close to the latter case. That is, the directionality of the type II staggered band offset (along the rod axis) between CdS and ZnSe that anisotropically surround the emitting CdSe center should induce a transition dipole along the rod axis. DHNRs lying mostly in-plane should then give rise to this transition dipole being oriented mainly parallel to the substrate. In-plane transition dipole

\[\text{Figure 4.12. A histogram of EQEs obtained from several DHNR-LEDs with and without F}_4\text{TCNQ.}\]
orientation is well known to reduce light outcoupling losses in OLEDs\textsuperscript{103–106} and similar effects should be taking place for our DHNR-LEDs. Variable angle spectroscopic ellipsometry\textsuperscript{101,105} indeed verify optical anisotropy in DHNR films. The complex refractive index of a DHNR film obtained from the uniaxial model is shown in Figure 4.14a. In particular, the ordinary (in-plane) extinction $k_o$ is significantly larger than the extraordinary (out-plane) extinction $k_e$. C/S QD films do not exhibit significant optical anisotropy (Figure 4.14b). The measured $k_o$ and $k_e$ values correspond to an orientation order parameter $[(k_e-k_o)/(k_e+2k_o)]$ of $-0.47$ for DHNRs and $-0.07$ for C/S QDs at 610 nm (near the emission wavelength) indicating that the transition dipole of DHNRs is nearly parallel to the substrate whereas that of C/S QDs are essentially randomly oriented. Therefore, we suggest that parallel orientation easily achieved for DHNRs and the resulting optical anisotropy significantly increase the upper limit of $\eta_{\text{out}}$, explaining the observed high EQE of 12%.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.13.png}
\caption{SEM images of (a) DHNR and (b) C/S QD films on Si wafer used in spectroscopic ellipsometry measurements and UV-Vis absorption spectra of the corresponding (c) DHNR and (d) C/S QD solutions.}
\end{figure}
Finally we note that there may be surrounding induced effects on the EL characteristics of C/S QDs and DHNRs that can complicate device performance analysis. For example, nearby metal surfaces and other factors can alter PL intensity and blinking, making it difficult to compare radiative recombination in devices to solution PL. A more directly important effect here may be the possibility of CdSe QDs being charged even at zero-bias due to charge transfer from ZnO/Al layers and there is evidence that EQEs of CdSe-based C/S QD-LEDs depend on the negative trion PL rather than the neutral exciton PL QY. While existing charges may help to explain the low, sub-band gap threshold voltages, EQE dependence on the trion PL makes estimates with solution PL inappropriate, even as an upper limit, in analyzing EQE. However, the apparent reduction in PL of charged QDs is a topic of continuing debate and a recent

![Figure 4.14. Variable angle spectroscopic ellipsometry results for determining nanorod alignment.](image)

Ordinary (in-plane) real ($n_o$) and imaginary ($k_o$) parts of the refractive index and extraordinary (out-of-plane) components, $n_e$ and $k_e$, measured by variable angle spectroscopic ellipsometry for (a) DHNR and (b) C/S QD films both spin-cast on Si wafer. SEM images of these two thin film samples used for ellipsometry along with their corresponding solution absorption spectra are shown in Figure 4.13.
study has shown that by suppressing nonradiative Auger recombination, trion PL can be as bright as exciton PL without the undesirable blinking behavior. Rod shape and directional type II band offset may help to suppress Auger recombination and therefore high EL from charged DHNRs may be possible. However, it may be more likely that F$_4$TCNQ is counteracting the charging effects of ZnO ETL/Al cathode. During the preparation of this paper we became aware of two recent reports demonstrating that either using an insulating PMMA layer between ZnO ETL and the emitting layer or controlling shell thickness in C/S QD-LEDs to reduce charging of QDs can lead to record-breaking LED performances (e.g., 20.5% EQE and >100,000 cd m$^{-2}$, respectively). These results are very impressive but the introduction of an insulating layer, whether in the form of a thin film or a shell on individual QDs, may lead to limitations especially in power efficiency. Our results using F$_4$TCNQ, if it also acted to counteract charging of C/S QDs and DHNRs, may be an alternative approach to this charging problem without compromising power efficiency (as suggested by the record efficiency of 34.6 lm W$^{-1}$ for red QD-based LEDs demonstrated here). Further work along these lines should provide insights that facilitate new and exciting means of designing and utilizing double heterojunctions to manipulate optical processes in colloidal QDs.

4.7. Summary

We have demonstrated LEDs incorporating our DHNRs as emissive layers. These devices exhibit narrow EL bandwidths, low threshold voltages, and stability under air operation. Given the recent finding of charging of CQDs from electron transport layer reducing device efficiencies (e.g., via multi-carrier Auger recombination), DHNRs with independently variable electron and hole injection barriers are excellent candidate materials for compensating or minimizing such loss mechanisms. Furthermore, we have demonstrated that the DHNR-LEDs in conjunction with an enhanced HTL can lead to remarkable LED performance in a conventional solution processed device structure. The benefits of introducing the hole dopant F$_4$TCNQ in the HTL are multifold including improved hole injection/transport and solvent
resistance and, possibly, reduced zero-bias charging of the emitters without sacrificing power efficiency. The anisotropic shape and the band offsets designed into the DHNRs allow improved carrier injection, low operating voltage, minimized energy transfer losses and enhanced light outcoupling. The DHNR-LEDs achieved here exhibit maximum brightness of 76,000 cd m\(^{-2}\), current efficiency of 27.5 cd A\(^{-1}\), and power efficiency of 34.6 lm W\(^{-1}\). A very high EQE of 12% at PL QY of only 40% implies that there is a fundamentally different and higher efficiency limit to these DHNR-LEDs than other C/S QD-based LEDs. It is the optical anisotropy of the DHNRs that should increase the upper limit on light outcoupling – a new and, until now, an unexplored aspect of these materials and their devices.

4.8. Experimental Details

**Materials:** Trioctylphosphine oxide (TOPO) (90%), trioctylphosphine (TOP) (90%), oleic acid (OA) (90%), trioctylamine (TOA) (90%), octadecene (ODE) (90%), 1-octanethiol (98.5%), CdO (99.5%), Zn acetate (99.99%), S powder (99.998%), and Se powder (99.99%) were obtained from Sigma Aldrich. N-octadecylphosphonic acid (ODPA) was obtained from PCI Synthesis. ACS grade chloroform and methanol were obtained from Fischer Scientific. All chemicals were used as received. Standard airless techniques were used in all syntheses.

**Synthesis of DHNRs:** CdS/CdSe/ZnSe DHNRs were synthesized following Ref. 15. Briefly, CdO powder (0.128 g) and ODPA (0.668 g) in TOPO (2.0 g) were degassed at 150 °C for 30 min then heated to 350 °C for 2 h. TOP:S (2.0 ml of 0.25 M solution) was quickly injected at 370 °C and stirred for 20 min at 330 °C. TOP:Se (1.0 ml of 0.25 M solution) was then slowly injected (4 ml h\(^{-1}\)). After 10 min, the reaction mixture was cooled to room temperature and the resulting CdS/CdSe nanorods were precipitated and redissolved in ~4 ml of chloroform. A mixture of Zn acetate (0.184 g) and OA (1.13 ml) in ODE (6 ml) were degassed and heated to 250 °C. After 1h, Zn containing reaction mixture was cooled to 60 °C and CdS/CdSe nanorod solution (2 ml) was injected. After heating to 250 °C, TOP:Se (1.0 ml of 0.25 M solution)
was slowly injected (4 ml h⁻¹). The reaction mixture was then heated to 300 °C for 5 min before cooling to room temperature.

**Synthesis of C/S QD:** CdSe/CdS/ZnS C/S QDs were prepared similar to a previous report. After degassing CdO powder (0.206 g) and OA (2.0 ml) in TOA (40 ml) at 150 °C for 30 min and heating to 300 °C, TOP:Se (0.4 ml of 1.0 M solution) was swiftly injected into the reaction mixture. After 45 sec, 1-octanethiol (0.21 ml) in TOA (6 ml) was slowly injected (1 ml min⁻¹). The reaction mixture was then allowed to stir for 30 min at 300 °C. 16 ml of Zn-oleate solution, prepared in a separate flask by stirring Zn acetate (0.92 g) and OA (3.2 ml) in TOA (20 ml) at 250 °C for 60 min, followed by 1.12 ml of 1-octanethiol in 6 ml of TOA were injected at 1 ml min⁻¹. After 30 min, the solution was cooled to room temperature.

**Device fabrication:** LEDs were fabricated on pre-patterned and pre-cleaned ITO on glass substrates (sheet resistance of 15~25 Ω square⁻¹). PEDOT:PSS (Clevios™ P VP AI 4083) was spincoated onto ITO (4000 rpm) and baked at 120 °C in air (5 min) and 180 °C in a glove box (15 min). Then 10 mg ml⁻¹ solution of TFB (H.W. Sands Corp.) in m-xylene or appropriate amount F₄TCNQ (Sigma-Aldrich) dissolved in 5 mg ml⁻¹ solution of TFB in m-xylene to achieve desired weight ratios was spin-coated (3000 rpm) and baked at 180 °C in a glove box (30 min). DHNRs (60 mg ml⁻¹) or C/S QDs (30 mg ml⁻¹) in chloroform after washing twice with 1:1 volume ratio of chloroform and ethanol were spin-cast (2000 rpm), then subsequently annealed at 180 °C in a glove box (30 min). ZnO (~30 mg ml⁻¹ in butanol, prepared following Ref. 15) was then spincoated (3,000 rpm) and annealed at 100 °C (30 min). 100 nm thick Al cathode was then deposited by electron-beam evaporation. LEDs were encapsulated with a cover glass using epoxy (NOA 86) in a glove box.

**Characterization:** TEM and SEM images were obtained on JEOL 2100 Cryo TEM and Hitachi S4800 SEM, respectively. UPS was performed using He I photon line (hv = 21.2 eV) at ~10⁻⁹ Torr (PHI 5400). Tapping-mode AFM and contact angle measurements were carried out on an Asylum Research MFP-3D AFM and a Rame-Hart model 500 goniometer/tensiometer, respectively. LED characteristics were recorded using a Spectrascan PR-655 spectroradiometer coupled with a Keithley 2602B source-
measure unit. EQE was calculated as the ratio of the number of photons emitted to the number of electrons injected. Current and power efficiencies were obtained as the ratio of the output luminance to the driving current density and the ratio of the luminous flux output to the driving electrical power, respectively. All device measurements were performed in air. UV-vis absorption spectra were obtained with an Agilent 8453 spectrometer. PL spectra were collected with Horiba Jobin Yvon FluoroMax-3. Ellipsometry of DHNR and C/S QD films on Si substrates were collected in the wavelength range of 400 - 900 nm at incidence angles of 50, 60 and 70° on a J. A. Woollam VASE Ellipsometer. Data analysis was performed using WVASE32 software. The thicknesses of the films were first determined using Cauchy model then Kramers–Kronig consistent model was used to calculate the optical constants. Anisotropic optical constants of the films were obtained using the uniaxial anisotropic model by minimizing the mean square error.
CHAPTER 5

DOUBLE-HETEROJUNCTION NANOROD BASED LIGHT-RESPONSIVE LIGHT-EMITTING DEVICES

Significant components of this chapter will be submitted as “Double-Heterojunction Nanorod Based Light-Responsive LEDs for Novel Display Applications” by Nuri Oh, Bong Hoon Kim, Seongyong Cho, John Rogers and Moonsub Shim.

5.1. Introduction

With increasing demand for complex, multifunctional electronics in light-weight and compact format, a dual ability to convert electricity into different forms of energy/signal including mechanical, thermal, and radiant and, conversely, to generate electrical energy/signal from these other forms is an attractive feature. In particular, the development of dual-functional display devices which can simultaneously transmit and receive information through visible light can provide a full real-time bidirectional communication, allowing for unique interfaces and interactivity with users and the devices. Of course, separate single-function devices (e.g., separate light emitting diodes (LEDs) with photodetectors (PDs)) can be integrated into systems that can perform two processes, but the design requires twice as many devices and a more complex fabrication process. Not surprisingly, every LED device can function as a PD. The interchangeability with III-V compound semiconductors based LED bulbs has been reported since it was first seriously proposed in the early 1970’s. However, epitaxial inorganic thin film diodes are not well-suited for high resolution displays that require large arrays of such devices, especially due to high cost, complexity of manufacturing and difficulty in scaling beyond the wafer size. Attempts have been made to develop two-way LED/PD operation in organic-based devices, but improving performance of one function usually leads to the degradation of the other. For example, donor-acceptor blends often used for efficient
charge separation in organic photovoltaics or PDs usually quench photoluminescence (PL) and therefore are unlikely to perform satisfactorily as electroluminescent materials in OLEDs.\textsuperscript{119,120}

Semiconductor nanocrystals, also referred to as colloidal quantum dots (QDs), have emerged as an important class of electroluminescent materials.\textsuperscript{5,6,76,77,121,122} Efficiencies and brightness of solution processed QD-LEDs\textsuperscript{123} rival those of vacuum deposited phosphorescent OLEDs and far outperform equivalently solution processed OLEDs.\textsuperscript{124} In addition, QD-LEDs exhibit much narrower bandwidth and smaller turn-on voltage.\textsuperscript{76,77} Colloidal QDs have also demonstrated potential in photovoltaics and PD applications.\textsuperscript{125,126} Given these advances and their size-tunable narrow-bandwidth emission and broadband absorption, colloidal QD-based devices may then be well suited for dual LED/PD operation. There have been many efforts, from materials to device level, to improve electroluminescence (EL) and photocurrent generation separately in QD-based devices. At the materials level, heterostructures of individual QDs have become essential for most optoelectronic applications. Type I straddling band offset, prototypical of core/shell (C/S) heterostructures, improves confinement of charge carriers and therefore enhance radiative recombination. Type II staggered band offset leads to efficient separation of photo-generated carriers, the first necessary step in photocurrent generation. However, as is the case in general, these approaches can optimize only one of two opposite processes, i.e., charge recombination vs. charge separation, and the improvement of one can be detrimental to the other.

Multiple heterojunctions can be incorporated into anisotropic nanocrystals in the form of nanorod heterostructures. In particular, double-heterojunction nanorods (DHNRs) contain type I heterojunctions with the smallest band gap semiconductor surrounded by two materials with type II band offset.\textsuperscript{15} Several advantages of DHNRs as electroluminescent materials in LEDs have recently been demonstrated.\textsuperscript{73} These advantages include enhanced light outcoupling due to their optical anisotropy, minimized energy transfer loss within the emitting layer, and independent control over electron and hole injection processes. The last benefit is especially appealing in that it can also apply to carrier extraction and therefore both charge separation and recombination can be fine-tuned within a single emitter material. Here, we show that DHNRs, acting as both charge separation center and emitter, can indeed simultaneously enable efficient photocurrent
generation and EL within a single device. With response time as fast as 300 µs, these devices operating under AC bias can detect external light sources while appearing to be continuously emitting bright light. These dual functioning, all solution-processed DHNR light-responsive LEDs open feasible routes to futuristic displays and related applications such as touchless interactive screens and massively parallel display-to-display data communication.

5.2. Dual Functionality of DHNR Light-Responsive LEDs

Figure 5.1 shows the energy band diagram and outlines the dual functionality of solution processed DHNR light-responsive LEDs. Simply changing from forward to reverse bias, these devices can be
switched between light emitting (red arrows) and light detecting (green arrows) modes, respectively. Solution absorption and PL spectra of DHNRs along with EL from a DHNR-LED are shown in Figure 5.1b. Similar to previous report, very narrow bandwidth (<30 nm), low turn-on voltage (~1.7 V) and high maximum brightness >60,000 cd/m² are observed. The small red shift in EL compared to PL at 5 V here is not present at lower biases (e.g., ~2V), indicating negligible energy transfer between DHNRs due to the separation of emitters at the tips of DHNRs. As shown in Figure 5.1c, these devices can be quite bright even at very low biases with high efficiencies (e.g., 4.3 % EQE at 1,000 cd/m² under 2.5 V bias and ~5% EQE at 5,000 cd/m² with 3V bias). These are especially useful considering that indoor display units only require a few hundred to ~1,000 cd/m² and extremely high brightness outdoor displays are in the mid thousands. As a point of comparison, similar wavelength red-emitting QD-LEDs of same device structure and fabricated under same conditions exhibit 3.1 % EQE at 1,000 cd/m² with 3.3 V and 2.4 % EQE at 5,000 cd/m² with 4.5 V. Furthermore, recently demonstrated > 30 lm/W luminous power efficacy of DHNR-LEDs surpass all red OLEDs and QD-LEDs in the practical brightness range around 1,000 cd/m².73

These DHNR LEDs with high brightness and efficiencies can also operate as useful PDs under reverse bias. Figure 5.1d and its inset show current density vs. voltage (J-V) characteristics of a DHNR light-responsive LED under green light illumination (532 nm, 5 mW) and in dark, respectively. Photocurrent to dark current ratio at zero bias is >10⁴. Under the same photoexcitation condition, DHNR-LEDs significantly outperform C/S QD devices. For example, at zero-bias, the photocurrent from DHNR-LEDs show more than 20-fold higher short-circuit current than C/S QD devices under same 532 nm incident light in Figure 5.1d. We believe it is precisely the optimization of EL that leads to poor performance for PD operation in the C/S QD case. That is, the wide band gap ZnS shell that enhances PL QYs desirable for EL causes a significant barrier for carrier extraction that leads to less photocurrent. Separate band alignments for electron and hole injection/extraction designed into DHNRs, on the other hand, facilitate both charge injection and extraction, allowing both LED and PD modes of operation to be efficient within one device.

Figure 5.1e shows the incident light power dependence of photocurrent for a light-responsive DHNR-LED at -2 V bias, demonstrating responsivity of ~22 mA/W for 532 nm irradiation. For 400 nm
excitation, we have observed responsivity as high as ~200 mA/W, a value approaching that of commercial Si photodiodes. The wavelength dependence of incident photon to current efficiency (IPCE) is shown in Figure 5.1f. The IPCE follows the absorption spectrum of DHNRs fairly well in the red near the CdSe band edge absorption region (inset). There is a small but measurable photocurrent beyond CdSe band edge absorption (> 650 nm), which may be arising from F$_4$TCNQ doping of TFB or from spatially separated charge transfer excitations across different layers. There is also a much faster increase in the IPCE than DHNR absorption spectrum beginning near 500 nm. This enhancement may be arising from the onset of contributions from the absorption in HTL with the double heterojunction facilitating the flow of photogenerated carriers. At shorter wavelengths, we expect photon absorption in ETL to also contribute, allowing for additional means for further improvements through the choice of charge transport layers.

To gain insights on how DHNRs enable efficient operation of both LED and PD modes, we have measured PL lifetime of DHNRs under bias in the light-responsive LED devices. Figures 5.2c and d compare the PL decay of DHNRs and C/S QDs at a small forward and reverse bias range where there is no contribution from electroluminescence. As shown in Figure 5.2c, C/S QDs do not exhibit a bias dependence whereas DHNRs show increasing PL lifetime with increasing forward bias. It has recently been shown that in C/S QD-LEDs, PL lifetime can increase with reverse bias because of charge transfer from ETL/cathode at zero bias. It has been suggested that this charge transfer leads to negative trions upon photoexcitation at zero and small forward bias causing faster PL lifetime whereas negative bias reduces the extra electrons leading to more contribution from neutral exciton recombination and therefore a longer PL lifetime. By introducing a barrier in the shell for electron transfer, this bias dependence of PL lifetime can be removed and our C/S QDs, which have ZnS shell with a significant electron barrier, show the expected PL lifetime that is independent of (small) external bias. However, DHNRs exhibit completely the opposite behavior of increasing PL lifetime with forward bias rather than reverse bias. This unexpected dependence is unlikely to be due to DHNRs being positively charged since there is a much larger barrier for hole transfer into the DHNRs. Rather, we believe it is the efficient extraction of photogenerated carriers (i.e., photocurrent) that leads to this behavior. The photocurrent contribution is evident when we compare PL lifetime of DHNRs
under zero bias and open circuit voltage conditions with when the device is electrically floating (i.e., actual open circuit). At zero bias, we observe a weight average PL lifetime of 23 ns. When the device is floating, DHNRs exhibit a significantly increased PL lifetime of 43 ns (black star in Figure 5.2e). This increased PL lifetime is almost exactly the same as when a forward bias of ~1.5 V is applied (the open circuit voltage of the light-responsive DHNR-LED where the photocurrent approaches zero). That is, when the two electrodes are shorted, photoexcitation leads to charge separation and photocurrent generation, causing PL lifetime to be significantly shorter whereas floating or open circuit voltage condition causes the potential drop from one electrode to the other that cancels the inherent driving force for photocurrent generation. As expected, C/S QDs with ZnS shell, which causes sufficient barriers for charge separation/extraction, do not exhibit such behavior. Hence, it is the double heterojunction that simultaneously enables both charge injection and extraction and therefore both LED and PD modes of operation.

Figure 5.2. Transient PL measurement for DHNR solution and DHNR-LEDs under bias. (a) PL decay of DHNR solution. (b) PL intensity at different wavelength at different time after 400 nm laser pulse. (c) PL decay of DHNRs and (d) C/S QDs at a small forward and reverse bias range where there is no contribution from electroluminescence. C/S QDs do not exhibit a bias dependence whereas DHNRs show increasing PL lifetime with increasing forward bias. (e) Weighted average PL lifetimes versus bias with DHNR- and C/S QD-LEDs.
Figure 5.3. Fast responsive and dual-functioning DHNR light-responsive LEDs. (a) Photocurrent measurement with green laser pulses. (b) Rise time and (c) fall time of the device as PD. (d) Schematic illustration of the device structure and dual mode operation of light-responsive display devices and energy band diagrams of the device. By alternating from a forward light emitting stage to the reverse light receiving stage, simultaneous light emission and light detection can be achieved. (e) The photograph of DHNR light-responsive LEDs under dual mode. Red light is emitting and green laser pulses irradiate the active pixel. (f) 0.3 ms wide rectangular voltage pulses for dual mode operation. The devices are alternatively emitting detecting light with the voltage pulses. After the end of the voltage pulses, photocurrent is recorded. A transient response of the photodetector under (g) green and (h) red laser pulses.
Given the above enabling aspects of the double heterojuctions designed into the DHNRs, we now discuss the time response of PD mode which is an important characteristics for many applications including displays and visible light communication. Figures 5.3a-c show the temporal response of a DHNR-LED operating in the PD mode. A 532 nm, 0.05 mW light source modulated by a mechanical chopper was incident on the light-responsive DHNR-LED with 20 ms duration at 25 Hz. The rise time and the decay time, defined as the time between 10% and 90% of maximum photocurrent, are ~0.3 ms and ~0.2 ms, respectively. Preliminary results using acousto-optically modulated light source indicate that 3 dB roll-off occurs around 10 kHz, suggesting that these DHNR-LEDs can be useful PDs down to time scales shorter than 0.1 ms.

Considering that the response time of commercial LCDs is around 1 to 2 ms, the sub-ms photocurrent response of our light-responsive DHNR-LEDs can enable new capabilities in LED-based display technologies. In particular, the sub-ms response time observed can allow detection of light with a device that appears to be emitting light continuously. Figure 5.3d shows a schematic of this dual mode of operation of our light-responsive DHNR-LEDs. By alternating from a forward-bias light emitting to reverse-bias light detecting modes within a ms time scale, these devices can receive signal while appearing to be continuously emitting light to the human eye. Figure 5.3e shows a photograph of a light-responsive DHNR-LED during this dual operation. Figure 5.3f shows the alternating voltage pulses of +3 V and -2 V, both with pulse width of 0.15 ms that were externally applied. During the alternating voltage, the photocurrent was measured at every -2 V duration while a 0.05 mW, 532 nm laser was incident on the device. Figure 5.3g shows the photocurrent response during this dual mode of operation. Supplementary movie S1 shows this measurement process and that the alternating bias does not cause the EL to appear blinking. These results ultimately demonstrate that DHNR-LEDs can be used as fast responsive PDs during light emission, in particular, demonstrating signal output while receiving information.
5.3. Demonstration of Light-Responsive LEDs

The dual functionality of our light-responsive DHNR-LEDs can impart further novel capabilities in display devices. As proof-of-concepts, we demonstrate 3 simple examples. The first example is demonstrated in Figures 4a where a 4 x 4 pixel array of DHNR-LEDs is irradiated by a laser pointer. The devices were integrated with a rudimentary commercial circuit board that was programmed to supply a forward bias of +5 V to DHNR-LEDs in the array once photocurrent is detected with any particular LED at zero bias. By scanning a laser pointer, spatially resolved signal is transmitted to the LED array and leads to a “writing” action on the “display.” Real time movie of this laser pointer writing process is shown in Supplementary Movie2. The second example shown in Figures 4b can be the basis for automatic brightness adjustment at the individual pixel level (e.g., useful for displays when different parts of the screen are under different lighting conditions such as being partly in the shade on a sunny day). As shown in Figure 5.4c and in Supplementary Movie3, by operating in the dual LED/PD mode, an individual pixel automatically adjusts brightness by responding to the intensity of external light (here, the distance to a white LED bulb was varied to adjust the intensity of the external light). The third example shown in Figure 5.4c and Supplementary Movie4 can be a means to enhance touch screens (or allow new touchless screens). The light-responsive DHNR-LED is shown to detect an approaching finger. The shadow formed by the finger under room light causes changes in the photocurrent detected by the DHNR-LED and the brightness of the device is adjusted accordingly.

The ability to function as both high-performance LED and PD arises from the double heterojunction band structure designed into the nanorods, allowing simultaneous enhancement of charge injection and charge separation within a single material. The three examples demonstrated above are only the beginning of many novel capabilities that can arise from our light-responsive DHNR-LEDs. With versatile solution processability (and high performance than can be maintained through solution processing), one can easily imagine a display consisting of a large array of light-responsive DHNR-LEDs. Such displays can communicate with each other through each pixel acting as both the light source and the detector, leading to
a massively parallel means of visible light data communication. Furthermore, these devices can operate not only as PDs but also as photovoltaics as shown in Figure 5.2. Hence, we can also envision harvesting of energy from sunlight or other ambient light sources as well as scavenging light lost from the display device itself through these light-responsive DHNR-LEDs.

Figure 5.4. Demonstrations of light-responsive LEDs. (a) Images showing the LED pixels are emitting light, once they detect light. (b) Images showing automatically controlled brightness as another LED bulb is approaching. (c) Images showing the brightness is changing as the finger is approaching the LED pixel.
5.4. Summary

In conclusion, we demonstrated bidirectional capabilities of light-responsive DHNR LEDs. The anisotropic geometry and staggered band offset have been shown to efficiently generate photocurrent. Fast response time enables AC operation of LED and PD modes together. The anisotropic shape and low band offset enhance the charge delocalization and charge separated states. The lowered energy barriers in DHNRs can lead to facile charge extraction to the charge transport layers. The capabilities suggested here can be applicable as futuristic display devices such as touchless interactive screens, self-powered display devices and extremely high speed display-to-display visible light communication.

5.5. Experimental Details

**Responsivity Measurement.** Photocurrent with different 1 mm radius and 532 nm wavelength laser was incident through an optical attenuator to vary the light intensity from 10μW to 100mW. The optical power of incident light was calibrated using an integrating sphere photodiode power sensor (Thorlabs, S140). I-V characteristics were obtained using a source meter (Keithley, 2602).

**Spectral response measurement:** Photocurrent at different wavelength were measured by a digital lock-in amplifier (Stanford Research Systems, SR830) with monochromatic illumination provided by a Xeon lamp passed through a monochromator (Jobin Yvon Horiba, FluoroMax-3). A bias of 0V or -2V was applied to light-responsive LED devices by the source meter and the illumination was mechanically chopped at ~100 Hz. The intensity of illumination at each wavelength was calibrated using a calibrated Si photodetector (Newport 71650).

**LED characteristics:** LED characteristics were recorded using a spectroradiometer (Spectrascan, PR-655) coupled with a source meter (Keithley, 2602). EQE was calculated as the ratio of the number of photons emitted to the number of electrons injected. Current and power efficiencies were obtained as the
ratio of the output luminance to the driving current density and the ratio of the luminous flux output to the driving electrical power, respectively. All device measurements were performed in air.

**4x4 device fabrication:** The device were fabricated on patterned ITO on glass substrates. PEDOT:PSS (Clevios P VP AI 4083) was coated onto ITO at 4000 rpm and annealed at 120 °C in air for 5 minutes. The device were transferred into a glove box and annealed at 180 °C for 20 minutes. Then, 7 mg/mL solution of TFB/F4TCNQ mixture dissolved in m-xylene was spin-coated at 3000 rpm and annealed at 180 °C for 30 min. DHNRs (~60 mg/mL) or C/S QDs (~30 mg/mL) in chloroform after washing twice with 1:1 volume ratio of chloroform and methanol was spin coated at 2000 rpm, then subsequently annealed at 180 °C for 30 minutes. 30 mg/mL solution of ZnO in butanol was then spin-coated at 3000 rpm and annealed at 100 °C for 30 minutes. A 100 nm thick Al cathode was then deposited by electron-beam evaporation technique. The device were encapsulated with a cover glass using epoxy (NOA 86) in a glovebox.

**Circuit board:** The commercially available Arduino Uno and Mega were used to control the devices for bidirectional display demonstrations. In addition to applying forward bias to turn on LED devices with the Arduino, it can measure the photocurrent and relay trigger signals from the external light sources. The board can be programmed with the Arduino Integrated Development Environment (IDE) software.
CHAPTER 6
I-III-VI COMPOUND SEMICONDUCTOR BASED CD-FREE DOUBLE-HETEROJUNCTION NANORODS

Significant components of this chapter will be submitted as “Direct Formation of Double-Heterostructure in I-III-VI2 Compound Semiconductor Nanorods” by Nuri Oh and Moonsub Shim.

6.1. Introduction

With respect to size tunability, narrow linewidth and high quantum yield (QY) of photoluminescence (PL), Cd-containing II-VI semiconductors are by far the highest performing colloidal quantum dots (QDs).26,127 These versatile solution-processable QDs impart capabilities that can allow the development of next-generation technologies in several broadly important areas including biomedical imaging,47 solid-state lighting128 and displays.73 However, concerns surrounding toxicity of Cd has limited their widespread adoption and their use in consumer products may soon be completely halted.129 For example, European Union's Restriction of Hazardous Substances Directive (RoHS), which restricts the level of Cd to be less than 100 ppm, has left most of the display industry without a viable material for continuing the path of advances paved by Cd-based QDs.129 InP has attracted the most attention as alternative to Cd-containing II-VI QDs but the performance metrics (e.g., linewidth and PL QY) fall short significantly.69,130 Furthermore, the more covalent nature of bonds in III-V materials than in II-VI semiconductors requires higher energy input (e.g., higher reaction temperature or more reactive reagents) that makes synthesis more costly and more difficult to optimize/improve. Cesium lead halide QDs are the most recent class of materials exhibiting tunable emission with high QYS but these materials also contain RoHS restricted element, namely Pb, and suffer from instability.35 Despite more than two decades of effort from an entire community of researchers, developing high performance non-toxic colloidal QDs remains one of the biggest challenges in the field.
While the search for Cd-based QD replacement continues, there have been advances beyond size-tunable, narrow linewidth, near unity QY PL. In particular, a variety of heterostructures of colloidal QDs, from type II staggered band offset core/shells to emerging anisotropic heterostructures, can allow new capabilities.\textsuperscript{7,50,52,131} Nanorod heterostructures (NRHs) with type II band offset allow efficient photoinduced charge separation and directionality useful in photovoltaics and photocatalysis.\textsuperscript{11,51} Double-heterojunction nanorods (DHNRs) have been shown to exhibit several advantages, including optical anisotropy and independent control over electron and hole injection processes.\textsuperscript{15} These salient features of DHNRs allow improvements in performance of QD-based LEDs while, at the same time, enabling additional function as photodetectors/photovoltaics. Hence, especially for optoelectronic device applications where carrier injection and/or extraction are of critical importance, there are many benefits and, more importantly, new capabilities that can be harnessed with Cd-free anisotropic nanorod heterostructures even without achieving <30 nm linewidth and 100% PL QY.\textsuperscript{73}

Colloidal QDs of I-III-VI\textsubscript{2} compound semiconductors, especially CuInS\textsubscript{2} and CuInSe\textsubscript{2} nanocrystals, have attracted much attention as Cd-free emissive materials.\textsuperscript{132,133} Despite the relatively broad emission linewidth that arises from lattice imperfections (i.e., vacancies, off-stoichiometry or surface defects), PL QYs of I-III-VI\textsubscript{2} nanocrystals can be made comparable to Cd-based materials through ZnS shell growth (or Zn incorporation (alloying) into vacancy sites or unnoticeable cation exchange with ZnS or ZnSe).\textsuperscript{134,135} I-III-VI\textsubscript{2} materials also have similar crystal structures as the II-VI semiconductors – i.e., replacing the sites for group II elements with group I and group III elements with essentially the same chalcogen framework. For I-III-VI\textsubscript{2} chalcopyrites, different bonding strengths and electrostatic forces between each cation and anion cause tetragonal distortion from the cubic zinc blende structure.\textsuperscript{136,137} Although thermodynamically not favored, the wurtzite equivalent structure can also be achieved with I-III-VI\textsubscript{2} semiconductors when two different cations are randomly distributed in the cation sites.\textsuperscript{138,139} Hence, directional growth in a manner similar to Cd-based II-VI nanorod formation should be feasible and, more generally, the extensive knowledge and understanding of heterostructure formation mechanisms in Cd-based semiconductors can
facilitate the synthesis of I-III-VI$_2$ NRHs.$^{15}$ Therefore, here we examine and develop Cd- and Pb-free I-III-VI$_2$ compound-based DHNRs. Interesting sawtooth-shaped and branched CuGaS$_2$/CuInSe$_2$ based NRHs are also achieved along the way.

6.2. Design of Cd-Free DHNRs

One recently demonstrated approach to I-III-VI$_2$ compound-based NRHs is a sequential cation exchange process from CdSe/CdS dot-in-rods to Cu$_2$Se/Cu$_2$S to CuInSe$_2$/CuInS$_2$ that retains the same morphology.$^{140}$ It is notable that these NRHs can emissive even after multiple cation exchange steps. However, the process is prone to impurities/defects that can degrade desired optical and electrical properties.$^{15}$ Furthermore, it may be difficult to achieve selectivity for different cations. For example, there is no obvious route to converting CdSe/CdS to CuInSe$_2$/CuGaS$_2$ since conditions that favor exchange of Cd in CdSe would also lead to exchange of Cd in CdS. Spatially varied cations in II-VI heterostructures would also likely be lost through cation exchange (e.g., cation exchange of CdSe/ZnSe would lead to both Cd and Zn being exchanged to a common set of cations). Hence, we have explored direct epitaxial solution growth of I-III-VI$_2$ NRHs and ultimately DHNRs.

Figure 6.1 shows the band alignment and Table 6.1 shows the lattice parameters of three candidate components for I-III-VI$_2$–based DHNRs along with other compositions explored here. The band gaps are bulk values as are the lattice parameters.$^{141,142}$ To achieve the desired DHNRs, we begin with CuGaS$_2$ NRs. Here, CuGaS$_2$ NRs provide the template for structural anisotropy and actively facilitate hole injection/extraction and electron blocking. CuInS$_2$ would become the emitter where electrons and holes would recombine. Considering quantum confinement effect, CuGaSe$_2$, CuInSe$_2$ and their alloys (including sulfides) may also have appropriate band gaps and offsets. Both AgGaS$_2$ and ZnSe have suitable band gaps and offsets for electron injection/extraction and hole blocking. For simply enhancing PL, ZnS would serve as a proper shell material.
6.3. Synthesis of CuGaS$_2$ Nanorods

In Cd-based semiconductors, the wurtzite structure is either energetically more favorable than the zinc blende structure or easily accessible at the nanometer dimensions, facilitating anisotropic growth. The main synthetic strategy for Cd-based DHNRs of CdS/CdSe/ZnSe combined preferential growth of CdSe along rod-axis of the seed wurtzite CdS NRs with selective shell growth of ZnSe on CdSe tips.$^{15}$ Similarly, we approach the synthesis of I-III-VI$_2$–based DHNRs starting from the formation of wurtzite CuGaS$_2$ NRs. Cu-based I-III-VI$_2$ semiconductors often grow from the copper sulfide (Cu$_{2-x}$S) seeds with hexagonal chalcocite and/or monoclinic djurleite structures.$^{143}$ The anions in Cu$_{2-x}$S maintain wurtzite-like scaffold, and therefore the resulting CuGaS$_2$ NRs can exhibit wurtzite structure. One of the most important
The requirement for achieving high-quality DHNRs is to synthesize uniform CuGaS$_2$ NRs (e.g., uniformity of nucleation and growth of the secondary components and minimizing the degree of inhomogeneous broadening in the resulting absorption/PL spectra).

CuGaS$_2$ NRs were synthesized by a heat-up method with Cu acetate and Ga acetylacetonate and 1-dodecanethiol (DDT), which was modified from the method of a previous report. The main difference from the literature was that DDT was used as the ligand and solvent instead of octadecene. Figure 6.2a shows the evolution of the UV-VIS absorption spectrum during CuGaS$_2$ NR growth. At 1 min, there is only an absorption tail which presumably corresponds to Cu$_{2-x}$S. As the reaction proceeds, the absorption peak at around 450 nm, corresponding to the band gap of CuGaS$_2$, clearly develops. TEM images in Figure 6.2b indicate that small dots become rod-shape nanocrystals at ~20 min of reaction time. TEM diffraction patterns clearly reveal the formation of wurtzite structure from ~5 min to 60 min, while the initial nanocrystals at 1 min do not show discernible peaks due to the low crystallinity or the presence of small particles. Based on these TEM images and diffraction patterns, we conclude that amorphous-like Cu$_{2-x}$S

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**Figure 6.2. Absorption spectra and TEM images of CuGaS$_2$ NRs.** (a) Absorption spectra during the growth of CuGaS$_2$ NRs. (b) TEM images and corresponding SAED patterns of CuGaS$_2$ NRs with different reaction times; 1 min, 5 min, 20 min and 60 min.
particles form first within a minute, then wurtzite CuGaS\(_2\) NRs which has a larger band gap around 2.66 eV successfully grow from these seeds.

### 6.4. Synthesis of CuGaS\(_2\)/CuInSe\(_2\) and CuGaS\(_2\)/CuInS\(_2\) NRHs

As the next step toward I-III-VI\(_2\)–based DHNRs, we have attempted to grow CuInS\(_2\) or CuInSe\(_2\) as emitting centers on CuGaS\(_2\) NRs. In ternary I-III-VI\(_2\) compound nanocrystals, it is well-known that the cation precursors for secondary component can alter the composition by inter-diffusion/substitution of cations in the lattice of the preexisting seed nanocrystals.\(^\text{140,143,144}\) Then a key challenge here is the inhibition of this undesirable cation diffusion by the selection of proper precursors or other reaction conditions. Metal oleates are one of the most common reagents for compound semiconductor nanocrystal synthesis and therefore we have first explored In-oleate and TOPSe as In and Se precursors. Pre-synthesized CuGaS\(_2\) NRs were purified and then transferred to the In-oleate/ODE solution. Slow addition of TOPSe at an elevated temperature led to the color of reaction mixture changing from yellow to reddish brown. Figure 6.3a shows corresponding change in the absorption spectrum. The increase of absorption tail in the wavelength region from 500 nm to 700 nm indicates that the secondary component of smaller band gap grows with increasing amount of Se precursor. TEM image in Figure 6.3b shows CuGaS\(_2\) seed NRs with typical length of ~40 nm and uniform width of 5 nm. Surprisingly, the introduction of In-oleate and TOPSe at 250 °C leads to the growth of sawtooth-like structures on the sides of CuGaS\(_2\) NRs as shown in the TEM images in Figures 6.3c-e. The inverse FFT and high resolution TEM image in Figure 6.3d reveal that the lattice constant of the secondary component is larger than that of CuGaS\(_2\). Based on the combination of elements used, the possible compositions of the secondary component can be CuGaS\(_2\), CuGaSe\(_2\), CuInS\(_2\) and CuInSe\(_2\). The lattice spacing shown in the Figure 6.3e best corresponds to CuInSe\(_2\), which has the largest lattice constant among the candidates (Table 6.1).
High resolution Z-contrast STEM analysis was also carried out to verify the composition of the sawtooth NRHs. A full-length image of the individual NR heterostructures in Figure 6.4a indicates that each protruding tooth from the CuGaS$_2$ NR has a higher Z-contrast and therefore consists of one or more heavier element than the main rod. Atomic column intensity analysis from STEM images similar to Figure 6.4c reveals that the intensities of the cation columns in the side protrusions are slightly brighter than those of the cation columns in the seed NR. However, the nature of mixed elements in the cation sites of I-III-VI$_2$ compound semiconductors makes the composition analysis somewhat difficult to ascertain. The intensity of anion columns diminishes from the side protrusion to the center of the rod, confirming that the anions in
the teeth are heavier than those of the main body of the rod, i.e., Se. For a more accurate determination of chemical composition of the heterostructures, EDS elemental mapping was carried out. Elemental maps in Figure 6.5 reveal that Ga and S are evenly spread throughout the center part of the NRs, while In and Se are concentrated in the secondary components protruding out on the side of the NRs. Hence we conclude that CuInSe$_2$ growth on the side of CuGaS$_2$ NRs.

**Figure 6.4. Z-contrast STEM image analysis.** (a) STEM image of an individual nanorod heterostructures. Each secondary component grown at the surface of CuGaS$_2$ nanorods shows higher Z-contrast than CuGaS$_2$ nanorods. (b) High resolution STEM images of the heterostructures. (c) Magnified images of the yellow dotted region in b. The side protrusions show higher Z-contrast anion columns which are indicated by red open circles, than the center component. The closer the anion columns to the center of the NR, the more diminished the Z-contrast.
In addition to CuInSe$_2$ growth, we have attempted to grow CuInS$_2$ on CuGaS$_2$ NRs. The introduction of In-oleate and ODE-S to CuGaS$_2$ NR solution at 250 °C led to similar sawtooth-like structures on the surface of CuGaS$_2$ NRs as shown in the absorption spectra and TEM images in Figure 6.6. The inverse FFT images and high resolution TEM images in Figure 6d reveal that the lattice constant of the secondary component are slightly larger than the one of CuGaS$_2$ but much smaller than CuInSe$_2$. The lattice parameter of the second phase is 6.40 Å, which is close to CuInS$_2$. Based on the smaller lattice mismatch

Figure 6.5. EDS elemental mapping of the CuGaS$_2$/CuInSe$_2$ nanorod heterostructures. (a) An entire picture of the nanocrystal with a yellow dotted box indicating scanned area. (b) EDS spectrum and element maps of (c) sulfur, (d) selenium, (e) combination of S and Se, (f) gallium, (g) indium and (h) combination of Ga and In. S and Ga are evenly distributed in the center part. Se and In are mainly distributed at the secondary component.

In addition to CuInSe$_2$ growth, we have attempted to grow CuInS$_2$ on CuGaS$_2$ NRs. The introduction of In-oleate and ODE-S to CuGaS$_2$ NR solution at 250 °C led to similar sawtooth-like structures on the surface of CuGaS$_2$ NRs as shown in the absorption spectra and TEM images in Figure 6.6. The inverse FFT images and high resolution TEM images in Figure 6d reveal that the lattice constant of the secondary component are slightly larger than the one of CuGaS$_2$ but much smaller than CuInSe$_2$. The lattice parameter of the second phase is 6.40 Å, which is close to CuInS$_2$. Based on the smaller lattice mismatch
to CuGaS₂ compared CuInSe₂, CuInS₂ can have larger interfacial area due to less strain at the interface with CuGaS₂ NRs. This lower strain effect is manifested in the growth of wider but small height of CuInS₂ growth than the dimensions of CuInS₂ growth on CuGaS₂ NRs.

The growth of CuInSe₂ (CuInS₂) side protrusions describe above is somewhat surprising in that only In and Se (S) precursors, and not Cu precursor, were added to purified CuGaS₂ NRs. However, as discussed in chapter 3, metal oleates can etch II-VI NRs and nanocrystals and a similar effect may be taking place here – i.e., In-oleate etching CuGaS₂ NRs and providing the necessary Cu precursor to grow CuInSe₂ or CuInS₂ upon Se or S precursor addition, respectively. As a control experiment we prepared purified

Figure 6.6. CuInS₂ growth on CuGaS₂ with ODE-S and Zn-oleate. (a) Absorption spectra during ODE injection in In-oleate solution. Strong absorption peak appears near 520 nm, which may correspond CuInS₂. (b), (c) Low-mag and (d) high-resolution TEM images of CuGaS₂ after injecting 0.2 mmol of ODE-S in In-oleate and CuGaS₂ NR solution. The lattice parameter of the second phase is 6.40 Å, which is close to CuInS₂. Based on the smaller lattice mismatch between CuGaS₂ and CuInS₂ than between CuGaS₂ and CuInSe₂, the secondary component which is grown on the side surface of CuGaS₂ can have longer interfacial area because it causes less strain and stress on CuGaS₂ NRs.

The growth of CuInSe₂ (CuInS₂) side protrusions describe above is somewhat surprising in that only In and Se (S) precursors, and not Cu precursor, were added to purified CuGaS₂ NRs. However, as discussed in chapter 3, metal oleates can etch II-VI NRs and nanocrystals and a similar effect may be taking place here – i.e., In-oleate etching CuGaS₂ NRs and providing the necessary Cu precursor to grow CuInSe₂ or CuInS₂ upon Se or S precursor addition, respectively. As a control experiment we prepared purified
CuGaS$_2$ NRs, injected them into Zn-oleate solution and left them to stir at 250 °C for 2 h. Figure 6.7a shows that the absorption spectrum does not change at all upon Zn-oleate treatment. However, there are obvious changes in the shape of the CuGaS$_2$ NRs as seen in TEM images of Figures 6.7b – e. While the CuGaS$_2$ NRs have sawtooth-like protrusions similar to NRHs of CuGaS$_2$ with CuInS$_2$ or CuInSe$_2$, the lattice parameters of the teeth and the main rod body were essentially identical. FFT pattern in Figure 6.7f also reveal that there are no separate peaks. These observations suggest that Zn-oleate etches the surface of CuGaS$_2$, especially side facets, and the etched ions (Cu$^+$, Ga$^{3+}$ and S$^{2-}$) can react causing regrowth or restructuring.
6.5. ZnS or ZnSe shell on CuGaS$_2$/CuInSe$_2$ NRHs for Double-Heterojunction Formation

As the final step for the formation of double heterostructures with Cd-free semiconductors, the shell growth on CuGaS$_2$/CuInSe$_2$ NRHs has been attempted by using Zn-oleate with sulfur or selenium precursors. First, ZnS shell growth was carried out with Zn-oleate and DDT to examine if PL from these NRHs can be enhanced/observed. Despite insignificant changes in both the absorption spectrum and the shape of NRHs upon growing ZnS shell, the result in Figure 6.8a shows a significant enhancement in PL intensity after introducing Zn and S precursors, indicating successful ZnS shell growth. The PL peak also blue shifts with reaction time. This blue-shift and the enhancement of PL suggest three possible scenarios; 1) Zn-oleate etches the CuInSe$_2$ and consequently the band gap increases due to effectively smaller size CuInSe$_2$,$^{69}$ 2) Zn ions are incorporated into the NRHs, causing alloying,$^{144}$ and 3) ZnS shell grows and causes compressive strain on the CuInSe$_2$ due to the large lattice mismatch causing an increase in the band gap.$^{132}$ A drastic improvement in PL is unlikely in the first scenario. The second mechanism would likely lead to a larger shift in PL and also alter the absorption spectrum significantly. Furthermore, the lattice parameter of the product (side protrusions) matches CuInSe$_2$ well whereas one might expect significant change in the lattice parameter upon alloying. Hence the last scenario of ZnS shell growth is the most likely and ZnS growth with continuous injection of Zn-oleate and DDT right after CuInSe$_2$ growth shows similar results, further supporting scenario 3.
To better understand their optical characteristics, absorption, PL, and PL excitation (PLE) spectra of CuGaS\textsubscript{2}/CuInSe\textsubscript{2}/ZnS NRHs (schematically shown in Figure 6.9a) were collected along with time-resolved PL. There is a strong absorption feature is at ~ 450 nm, corresponding to band gap of CuGaS\textsubscript{2} NRs. The emission peak is at ~ 700 nm, corresponding to a large (pseudo) Stokes shift (Figure 6.9b). The PLE spectrum is essentially identical to the absorption spectrum which supports the formation of epitaxial CuGaS\textsubscript{2}/CuInSe\textsubscript{2}/ZnS NRHs – i.e., high yield of PL from CuInSe\textsubscript{2} even when photons are absorbed in the CuGaS\textsubscript{2} part. Time-resolved PL measurements show multi-exponential decay. In Figures 6.9c and d, \( \tau_n \) indicates the lifetime of each decay component \( n \) and the number inside the parenthesis shows the respective
fractional intensity. Three-exponential fitting leads to around 10% of 16 ns component, 50% of 126 ns, and 41% of 600 ns. The highest fractional intensity component shows ~100 – 200 ns time constant similar to the reported values of conventional I-III-VI₂ nanocrystals. It is notable that these NRHs exhibit extremely long PL lifetime of 600 ns with nearly as high fractional intensity. Following results of delayed PL with C/S QDs, nanoplatelets and Cd-based DHNRs in previous chapter, we suggest that the rod-geometry may be increasing PL lifetime by delocalizing photogenerated carriers throughout the nanorod.

Figure 6.9. PLE and Time resolved PL measurement. (a) Schematic illustration of the CuGaS₂/CuInSe₂/ZnS DHNRs. (b) Absorption, PL (excitation with 450 nm light) and photoluminescence excitation (PLE) (emission intensity measured at 700 nm) spectra. The PLE curve is identical to the absorption which indicates that the considerable amount of charges which contribute the radiative recombination result from the CuGaS₂ absorption and the charge transfer to the secondary component, CuInSe₂. (c), (d) PL decay curves and tri-exponential fitting for short and long time periods, respectively.
Finally, we have attempted to grow ZnSe on CuGaS₂/CuInSe₂ NRHs in order to form the second interface of the double-heterojunction. Purified CuGaS₂/CuInSe₂ NRHs were injected into Zn-oleate solution and then TOPSe precursors were added slowly (see experimental details). Figure 6.10a shows the appearance of a PL peak around 720 nm after growing ZnSe shell. This peak position is slightly red-shifted.
from the case with ZnS shell presumably due to the smaller band offset of ZnSe with CuInSe₂ causing more spreading of the electron wave function to the shell. TEM images in Figures 6.10 b-e clearly show the change of the size of the secondary component. The lattice mismatch between CuInSe₂ and ZnSe is only 2 % and this small mismatch can induce more favorable nucleation and growth. Despite the intention of growing very thick ZnSe shell, surprisingly, long third component on CuInSe₂ side protrusions are observed (Figure 6.10h and i). Thus, we confirmed successfully grown ZnSe shell and ultimately achieved Cd-free DHNRs with photoluminescence.

6.6. Summary

In summary, we have successfully synthesized Cd-free luminescent DHNRs with I-III-VI₂ compound semiconductors. By introducing metal oleate, we observed the same etching and re-growing effect as we showed in the previous chapters. Facilitating those metal oleate in I-III-VI₂ semiconductors enables to achieve the direct formation of heterostructures with CuInS₂ and CuInSe₂ on CuGaS₂ NRs, which has not been reported yet anywhere to the best of our knowledge. Interesting sawtooth structures has been analyzed with high resolution TEM, STEM and EDS. After growing ZnSe or ZnS shell on the CuGaS₂/CuInSe₂ NRHs distinct PL and other interesting/useful optical properties, including large Stokes shift, charge transfer between components, and long lived excitons, were observed.

6.7. Experimental Details

Materials. Trioctylphosphine oxide (TOPO) (90%), trioctylphosphine (TOP) (90%), oleic acid (90%), oleylamine (OAm) (70%), octadecene (ODE) (90%), CdO (99.5%), copper (I) acetate (Cu(ac)) (99.99%), gallium acetylacetonate (Ga(acac)₃) (99.99%), In (III) acetate (In(ac)₃) (99.99%), zinc acetate (Zn(ac)₂) (99.99%), 1-dodecanethiol (DDT), sulfur (99.998%), and selenium (99.99%) were obtained from Sigma Aldrich. Sodium oleate (Na-oleate) (>97%) was obtained from Tokyo Chemical Industry. N-
octadecylphosphonic acid (ODPA) was obtained from PCI Synthesis. ACS grade chloroform and methanol were obtained from Fischer Scientific. All chemicals were used as received.

**Synthesis of CuGaS$_2$ seed NRs:** Cu(ac) (0.2 mmol) and Ga(acac)$_3$ (0.2mmol) in 5 ml of DDT was magnetically in a 50-ml three-neck round-bottom flask. The mixture was degassed under N$_2$ flow and heated to 240 °C at a rate of 30 °C/min. The yellow solution became clear and then changed to deep yellow solution. The reaction was terminated by cooling to room temperature. The final solution was dissolved in chloroform, centrifuged at 2000 rpm. The precipitate was re-dissolved in chloroform, and then prepared as a solution for the next step.

**Synthesis of CuGaS$_2$/CuInS$_2$ NRHs:** A mixture of In(ac)$_3$ (0.2 mmol) and oleic acid (0.6 mmol) in 3 mL of ODE were prepared in a 25 mL three-neck round-bottom flask and degassed at 120 °C for 30 min under vacuum. The solution was then heated to 250 °C under N$_2$ atmosphere to form In-oleate. After 1 hour, the In-oleate solution was cooled to 60 °C. A purified solution of CuGaS$_2$ NR seeds was injected into the solution and chloroform was allowed to evaporate for 30 min under vacuum. After heating to 180 °C, 1ml of 0.2M ODE-S solution was slowly injected at 250 °C at a rate of 8 mL/hr and the reaction mixture was allowed to stir at 180 °C for 5 min prior to cooling to room temperature. The final solution was dissolved in chloroform, centrifuged at 2000 rpm. The precipitate was re-dissolved in chloroform, and then prepared as a solution for the next step.

**Synthesis of CuGaS$_2$/CuInSe$_2$/ZnS DHNRs:** A mixture of Zn(ac)$_2$ (0.5 mmol) and oleic acid (1.0 mmol) in 3 mL of ODE were prepared in a 25 mL three-neck round-bottom flask and degassed at 120 °C for 30 min under vacuum. The solution was then heated to 250 °C under N$_2$ atmosphere to form Zn-oleate. After 1 hour, the Zn-oleate solution was cooled to 60 °C. A purified solution of CuGaS$_2$/CuInSe$_2$ NRH seeds was injected into the solution and chloroform was allowed to evaporate for 30 min under vacuum. Then, 3 mL of DDT, 1 mL of TOP and 0.5 mL of oleylamine were injected to the reaction flask. After heating to 250 °C, the reaction mixture was allowed to stir at 250 °C for 10 hours prior to cooling to room temperature. The final solution was dissolved in chloroform, centrifuged at 2000 rpm.
Synthesis of CuGaS$_2$/CuInSe$_2$/ZnSe DHNRs: A mixture of Zn(ac)$_2$ (0.5 mmol) and oleic acid (1.0 mmol) in 3mL of ODE were prepared in a 25 mL three-neck round-bottom flask and degassed at 120 °C for 30 min under vacuum. The solution was then heated to 250 °C under N$_2$ atmosphere to form Zn-oleate. After 1 hour, the Zn-oleate solution was cooled to 60 °C. A purified solution of CuGaS$_2$/CuInSe$_2$ NRH seeds was injected into the solution and chloroform was allowed to evaporate for 30 min under vacuum. After heating to 250 °C, TOPSe solution containing 20 mg of Se in 1.0 mL of TOP was slowly injected at 250 °C at a rate of 4 mL/hr and the reaction mixture was allowed to stir at 250 °C for 5 min prior to cooling to room temperature. The final solution was dissolved in chloroform, centrifuged at 2000 rpm. The precipitate was re-dissolved in chloroform, and then prepared for the analyses with TEM and optical properties measurement.

Characterization. TEM samples were prepared on Au grids with thin carbon film from a dilute solution of NCs in chloroform. TEM analysis was carried out with a JEOL 2100 TEM operating at 200 kV. EDS and STEM analyses were carried out with a JEOL JEM-2200FS aberration-corrected STEM/TEM operating at 200 kV. UV-vis absorption spectra were obtained with an Agilent 8453 photodiode array spectrometer. PL spectra were collected with a Horiba Jobin Yvon FluoroMax-3 spectrofluorometer. PL lifetime were collected with a Horiba Jobin Yvon Nanolog.
CHAPTER 7
SUMMARY AND FUTURE WORK

We have successfully developed the DHNRs as a new subclass of nanocrystals that incorporate both type I and type II band offsets where the heterojunctions are active rather than passive insulators. Our unique strategy to extend anisotropic nanocrystal growth to introduce the double-heterojunction enables to develop multi-component, multi-functional heterostructures. Band offsets designed into the nanorods can facilitate both charge recombination and separation and the anisotropic shape enhances light outcoupling and collection, ultimately allowing one device to function as both high performance LED and PD. These dual functioning, all solution-processed DHNR light-responsive LEDs open feasible routes to futuristic displays and related applications such as touchless interactive screens, self-powered display devices and massively parallel display-to-display data communication. Building on our simple strategy to extend anisotropic nanorod growth to introduce the double heterojunction (while maintaining narrow size distribution) should pave the path for developing application-specific design and synthesis of multi-component, multi-functional heterostructured nanocrystals.

In this thesis, several areas appear to hold great potential for future research;

a) newly developed synthesis procedures for both Cd-based and Cd-free DHNRs,

b) characterization techniques identifying the heterointerfaces with near atomic precision,

c) correlation of charge carrier dynamics with electronic structures of DHNR,

d) and novel device applications.

Based on the knowledge obtained from this thesis, some future work can be suggested;

i) synthesis of green light emitting DHNRs by adjusting the composition or size of the CdSe core

ii) PL enhancement through the synthesis optimization of I-III-VI semiconductor DHNRs
iii) III-V semiconductor based DHNRs (AlP/InP/GaP)
iv) alignment of DHNRs either vertically or horizontally with optical anisotropy measurement
v) cascade heterojunction nanorods for better charge separation
vi) transient EL and transient photocurrent measurement of light-responsive LEDs
vii) transient studies of carrier dynamics for efficient charge extraction and recombination
viii) and touchless interactive screens, self-powered display devices and massively parallel display-to-display data communication

Some preliminary data about the future work suggested above is provided in Appendix. It is my sincere hope that this work would provide some useful insights for future researchers to develop even more fascinating multifunctional nanocrystals and their applications.
REFERENCES


[18] McDaniel, H.; Zuo, J.-M.; Shim, M. Anisotropic Strain-Induced Curvature in Type-II CdSe/CdTe


APPENDIX

Appendix A. Synthesis of Green Light Emitting DHNRs

Figure A1 shows yellow light emitting DHNRs. Purer TOPO (99%) causes smaller diameter of CdS and consequently grows smaller size of CdSe than 90% TOPO. However, further size tuning or composition change is required to obtain green light emitting DHNRs. Figure A2 shows two strategies of green DHNRs. We believe the two different tips provide different type of heterojunctions; CdSe$_{1-x}$S$_x$ alloy tips and small CdSe tips may form type II heterojunction and type I heterojunction with CdS, respectively.

Figure A1. Yellow light (580 nm) emitting DHNRs. Small size of CdS and CdSe leads yellow light emission after growing ZnSe shell.

Figure A2. Two main strategies. Alloy core vs. small CdSe core.
Appendix B. Angle Dependent PL

Our efforts in the chapter 4 have included measurements elucidating optical anisotropy of nanocrystal/NR films. A promising approach is the angle dependent PL (Figure B1). The DHNRs can possess the transition dipoles along their rod axis so that we can confirm their alignment by measuring the resultant emission polarization. Basically, materials with random transition dipole orientation can be treated as a superposition of $p_x$, $p_y$ and $p_z$-dipoles (one third each). Materials with horizontally oriented dipoles (but random in-plane) are considered as consisting of one half of $p_x$- and one half of $p_y$-dipoles. Without loss of generality, the $x$-$z$-plane is considered as the plane of observation, leading to the implication that the $p_y$-dipoles emit only $s$-polarized light whereas the $p_x$- and $p_z$-dipoles are responsible for the $p$-polarized emission. Consequently, the analysis of the $p$-polarized emission can yield information about the existence of vertical dipoles. Taking into account that dipoles radiate strongest perpendicular to their direction of oscillation, the $p_z$-dipoles emit mainly at large angles of $\phi$ (close to 90°). A schematic illustration of the measurement setup is shown in Figure B2.

The preliminary data in Figure B3 shows the difference of PL intensities from C/S QD films, Dot-in-rod (DiR) films and DHNR films. Given the isotropic structure of C/S QDs and the isotropic alignment of DiRs, they appear consistent with random dipole orientation. However, staggered band offset of DHNRs causes asymmetric separation of hole and electron wave functions so that it causes the transition dipoles along the rod axis. As long as the NRs are horizontally aligned on the substrate, the transition dipoles would be parallel to the substrate as well. At high angles of $\phi > 50$ degrees, DHNRs do not show high PL intensity while C/S QDs do as shown in Figure B3. As discussed above, z-dipole contribution is more dominant in this regime. Thus, we can assume that the one which showed lower intensity at high angle have more horizontally aligned transition dipoles. Additional experiments are in progress to further elucidate the relationship between the geometric structure of nanocrystals, the orientation of transition dipoles and light outcoupling efficiencies.
Figure B1. Schematic illustration of angle dependent PL measurement. The angle of incidence is 45 degrees with the substrate, which enables to uniformly excite both vertically and horizontally oriented nanorods. Detector collects p-polarized light from the samples. More nanorods horizontally aligned contribute the emission intensity for low φ angle, and higher emission intensity from vertical nanorods can be collected at higher φ angle.
Figure B2. Schematic illustration of the instrument setup for angle dependent PL measurement.

Figure B3. Angle dependent PL of C/S QDs, Dot-in-Rods and DHNRs. Angle-dependent PL intensities of the p-polarized light from C/S QD, DiR and DHNR films on glass substrates.
Appendix C. III-V Semiconductor Based DHNRs (AlP/InP/GaP)

Figure C1. Design of III-V semiconductor based DHNRs (or double-heterojunction nanocrystals).
Appendix D. Vertical or Horizontal Alignment of Nanorods

Figure D1. Alignment of DiR on TEM grids. This work was done with Deepa Kote.
Appendix E. Cascade Heterojunction Nanorods for Better Charge Separation

Figure E1. Energy band diagram and TEM images of CdS/CdTe/ZnTe cascade heterojunction nanorods.

Figure E2. Proof-of-concept photovoltaic device characteristics.
Appendix F. Transient EL Measurement of Light-Responsive LEDs

Figure F1. Transient EL curves with QD-LEDs and DHNR-LEDs.
Appendix G. Movies for Light-Responsive LEDs

The movies for showing the operation of Light-Responsive DHNR-LEDs that has been presented in this thesis may be found in supplemental files named Movie1.mp4, Movie2.mp4, Movie3.mp4 and Movie4.mp4.

Movie1: 2 by 2 pixel arrays of DHNR-LED devices, irradiated by a commercial blue led bulb

Movie2: 4 by 4 pixel arrays of DHNR-LED devices, irradiated by a commercial green laser pointer

Movie3: DHNR-LEDs to automatically adjust the brightness depending on the brightness of the external light source

Movie4: DHNR-LEDs to detect an approaching finger