Exploring the surface of semiconductor nanocrystals: Optical properties and Applications

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Abstract

This thesis aims to understand the optical properties of small sized semiconductor NCs that exhibit intrinsic dual emission (core and surface). To study the size dependence of small NCs, a set of CdSe NCs with sizes ranging from 0.89 to 1.66 nm in radius were synthesized. The study confirms that as the nanocrystals become small, the surface emission strongly increases in amplitude, and the core emission broadens and red-shifts. These effects are rationalized in terms of coupling to ligands via electron transfer theory. The transition from the QD to the molecular cluster regime is found to be at 1.2 nm radius, in contrast to the transition from the bulk to QD transition at the Bohr radius of 5.4 nm in CdSe. These size-dependent surface electronic phenomena may be used for light emission applications. Further, the emissive properties of thiol-capped CdSe NCs are investigated through temperature-dependent PL measurements. This thesis demonstrates the influence of thiols on the relative PL intensities of the core and surface emissive states, as well as on the observed Stokes shifts. A redshift of both the core and surface PL in comparison with phosphonate-capped NCs is confirmed with literature, exploring the effect of thiols as excitonic hole-delocalizing ligands. In the end, the thesis describes the application of these NCs in optical nanothermometry. By chemical control of the thermodynamics of the core and surface emission, these nanocrystals support ratiometric temperature sensing over a broad temperature scale.

Résumé

Cette thèse vise à comprendre les propriétés optiques de petites nanocristaux (NC) semi-conductrices présentant une double émission intrinsèque (noyau et surface). Pour étudier la dépendance à la taille de petites NC, nous avons synthétisé un ensemble de NC CdSe avec des tailles allant de 0,89 à 1,66 nm de rayon. L'étude confirme que lorsque les nanocristaux deviennent petits, l'émission de surface augmente fortement en amplitude, et l'émission de noyau s'élargit et déplace à des énergies plus basses. Ces effets sont rationalisés en termes de couplage aux ligands via la théorie du transfert d'électrons. La transition entre le régime QD et le cluster moléculaire se situe à un rayon de 1,2 nm, contrairement à la transition entre la masse et la transition QD au rayon de Bohr de 5,4 nm dans CdSe. Les phénomènes dépendant de la taille peuvent être utilisés pour des applications d'émission de lumière. De plus, les propriétés émissives des NC de CdSe encapsulés par thiol sont étudiées par des mesures de PL dépendant de la température. Cette thèse démontre l'influence des thiols sur les intensités PL relatives des états émissifs de la noyau et de la surface, ainsi que sur les décalages de Stokes observés. Un décalage vers le rouge à la fois du noyau et de la PL surface par rapport aux NC encapsulés par des phosphonates est confirmé par la littérature, explorant l'effet des thiols en tant que ligands excitoniques délocalisant les trous. Au final, la thèse décrit l'application de ces NC en nanothermométrie optique. Par le contrôle chimique

de la thermodynamique de l'émission de noyau et de surface, ces NCs supportent la détection de température ratiométrique sur une large échelle de température.

TABLE OF CONTENTS

Abstract2
Résumé3
Table of Contents 5
List of Figures
List of Tables
Preface and Contribution of Authors
List of Abbreviations
Acknowledgements
Chapter 127
Colloidal Semiconductor NCs
1.1 Introduction
1.2 Quantum Size Effect in Semiconductor NCs
1.3 Semiconductor NC as "Particle in a Box"
1.4 Composition of Semiconductor NCs
1.5 Surface of NCs
1.5 Surface of NCs421.6 Linear Spectroscopy of CdSe Nanocrystals45
1.5 Surface of NCs421.6 Linear Spectroscopy of CdSe Nanocrystals451.7 White light Emission from Semiconductor NCs47
 1.5 Surface of NCs
1.5 Surface of NCs421.6 Linear Spectroscopy of CdSe Nanocrystals451.7 White light Emission from Semiconductor NCs471.8 Semiclassical Marcus-Jortner Electron Transfer Theory – Prior work521.9 Conclusion57
1.5 Surface of NCs421.6 Linear Spectroscopy of CdSe Nanocrystals451.7 White light Emission from Semiconductor NCs471.8 Semiclassical Marcus-Jortner Electron Transfer Theory – Prior work521.9 Conclusion57References59
1.5 Surface of NCs421.6 Linear Spectroscopy of CdSe Nanocrystals451.7 White light Emission from Semiconductor NCs471.8 Semiclassical Marcus-Jortner Electron Transfer Theory – Prior work521.9 Conclusion57References59Chapter 277
1.5 Surface of NCs421.6 Linear Spectroscopy of CdSe Nanocrystals451.7 White light Emission from Semiconductor NCs471.8 Semiclassical Marcus-Jortner Electron Transfer Theory – Prior work521.9 Conclusion57References59Chapter 277Synthesis and characterization of semiconductor nanocrystals approaching the molecular cluster limit77
1.5 Surface of NCs421.6 Linear Spectroscopy of CdSe Nanocrystals451.7 White light Emission from Semiconductor NCs471.8 Semiclassical Marcus-Jortner Electron Transfer Theory – Prior work521.9 Conclusion57References59Chapter 277Synthesis and characterization of semiconductor nanocrystals approaching the molecular cluster limit772.1 Introduction78
1.5 Surface of NCs421.6 Linear Spectroscopy of CdSe Nanocrystals451.7 White light Emission from Semiconductor NCs471.8 Semiclassical Marcus-Jortner Electron Transfer Theory – Prior work521.9 Conclusion57References59Chapter 277Synthesis and characterization of semiconductor nanocrystals approaching the molecular cluster limit772.1 Introduction782.2 Nanocrystal Synthesis80
1.5 Surface of NCs421.6 Linear Spectroscopy of CdSe Nanocrystals451.7 White light Emission from Semiconductor NCs471.8 Semiclassical Marcus-Jortner Electron Transfer Theory – Prior work521.9 Conclusion57References59Chapter 277Synthesis and characterization of semiconductor nanocrystals approaching the molecular cluster limit772.1 Introduction782.2 Nanocrystal Synthesis802.3 Nanocrystal characterization and techniques82
1.5 Surface of NCs421.6 Linear Spectroscopy of CdSe Nanocrystals451.7 White light Emission from Semiconductor NCs471.8 Semiclassical Marcus-Jortner Electron Transfer Theory – Prior work521.9 Conclusion57References59Chapter 277Synthesis and characterization of semiconductor nanocrystals approaching the molecular cluster limit772.1 Introduction782.2 Nanocrystal Synthesis802.3 Nanocrystal characterization and techniques822.4 Ligand Exchange84

2.6 Time Correlated Single Photon Counting (TCSPC)	
2.7 Transmission electron microscopy (TEM)	
2.8 X-ray photoelectron spectroscopy (XPS)	
2.9 Resonance Raman Spectroscopy	
References	91
Chapter 3	97
Extending Semiconductor Nanocrystals from The Quantum Dot Regim Molecular Cluster Regime.	e to The 97
3.1 Introduction	
3.2 Results and Discussion	100
3.3 Conclusion	109
References	111
Chapter 4	118
The effect of Exciton-Delocalizing Thiols on Intrinsic Dual Emitting Semiconductor Nanocrystals	118
4.1 Introduction	119
4.2 Results and Discussion	120
4.3 Conclusion	133
References	134
Chapter 5	141
Towards Ratiometric Nanothermometry via Intrinsic Dual Emission fro Semiconductor Nanocrystals	om 141
3.1 Introduction	142
3.2 Results and Discussion	144
3.3 Conclusion	151
References	152
Chapter 6	155
Summary, Conclusions and Future Work	155
References	160
Appendix A	161
Supplementary Information	161

A.1 Supplementary information for Chapter 3	161
A.2 Supplementary information for Chapter 4	170
A.3 Supplementary information for Chapter 5	175
References:	177

LIST OF FIGURES

Figure 1.5 Nanocrystal ligand binding motifs according to the covalent bond
classification method ⁴² Reprinted with permission from reference 42. Copyright
© 2013 American Chemical Society
Figure 1.6 Absorption and PL spectra of CdSe NC 46
Figure 1.7 Tunability of emission wavelength of NCs based on the size
Figure 1.8 White light emission spectra. White light emitting CdSe NCs compared
to regular large sized NCs (inset)
Figure 1.9 Three different models to explain temperature dependent PL: (a) The

Figure 2.5 TEM for a) synthesized CdSe NC b) small commercial CdSe NCs...87

Figure 3.4 Thermodynamics rationalizes the surface PL, and the transition point. The transition radius is ~ 1.2 nm for 300K. a) Integrated areas of the surface band relative to the total PL emission, A_S/A_T as a function of radius, R. b) Temperature dependence of A_S/A_T for different sized NCs c), Calculation showing

Figure 4.3 a) Temperature dependent ratio of Integrated areas of Surface and Core emission b) simulation of change in surface to core ratio with different $\Box G$

values. Reprinted with permission from Jethi et al., "The effect of Exciton-Delocalizing Thiols on Intrinsic Dual Emitting Semiconductor Nanocrystals", ChemPhysChem 2016, 17, 665. Copyright © 2016 WILEY-VCH Verlag GmbH & Figure 4.4 a) Relative integrated surface intensities with respect to room temperature before (TOP) and after ligand exchange(DDT/ADMT), Temperature dependent PL normalized to surface emission b) TOP, c) ADMT, d) DDT showing the blue-shift in the surface state as the temperature is reduced to 80K. Reprinted with permission from Jethi et al., "The effect of Exciton-Delocalizing Thiols on Intrinsic Dual Emitting Semiconductor Nanocrystals", ChemPhysChem 2016, 17, 665. Copyright © 2016 WILEY-VCH Verlag GmbH &

Figure 5.2 (a) Dual emission from a CdSe semiconductor nanocrystal. The size and chemical passivation was optimized for contrast over a wide temperature range. (b) The integrated area of the surface photoluminescence (PL) band relative to band edge exciton PL from the core of the nanocrystal. The points are data and the line is a polynomial fit. The inset shows the residual differences between the data and the fit. Reprinted with permission from Jethi et al., "Towards Ratiometric Nanothermometry via Intrinsic Dual Emission from

Figure S3.5 PL QY for different sized NCs 168

Figure S3.6 Absorption spectra for different sized NCs 169

Figure S4.1 XPS data for TOP capped dots171

Figure S4.2 XPS data for ADMT capped dots 172

Figure S4. 3 XPS data for DDT capped dots......173

Figure S5. 2 Aging effect or	sample 1	176
------------------------------	----------	-----

Figure	S5.3 Aging	effect on	Sample 2		76
Inguic	00.0 1161116	chect off	Sample 2	······································	U

LIST OF TABLES

Table 1. 1 Semiconductor NC market and applications 32
Table 4. 1 Room temperature fluorescence data for dual emitting CdSe NCs
passivated with TOP/ADMT/DDT123
Table 4.2 dE/dT values for surface and core emission blue-shift for dual emitting
CdSe NCs passivated with TOP/ADMT/DDT 130
Table S4.1 Calculated Energy of the Highest Occupied Molecular Orbital (HOMO)
by Density Functional Theory170

PREFACE AND CONTRIBUTION OF AUTHORS

This thesis contributes originally to understand the properties of small NCs. The author claims that it brings distinct contribution to knowledge about behavior of small CdSe NCs depending on their size and capping ligands. Chapter 1 is the introduction chapter that presents important literature and theory on CdSe NCs in general. It also discusses the prior work done by the Kambhampati group to create a better understating of the following chapters.

Chapter 2, the experimental section describes all the techniques used to acquire data and perform analysis on the NC samples. This chapter is based on the article "Synthesis and characterization of semiconductor nanocrystals approaching the molecular cluster limit" which has been submitted to a peer reviewed journal for publication.

Chapter 3 is based on the article "Extending Semiconductor Nanocrystals from The Quantum Dot Regime to The Molecular Cluster Regime", published in "The Journal of Physical Chemistry C" in 2017. This chapter shows the size dependence of small NCs. It describes the size dependent transition of NCs in the molecular regime and rationalized it in terms of surface free energy. It builds upon the prior work done by Kambhampati group related to the semi-classical Marcus Jortner theory. The materials were synthesized by Lakshay Jethi. The linear spectroscopy and low temperature cryo-PL data was acquired by Lakshay Jethi. The modelling calculations were performed by Timothy G. Mack. The manuscript was written by Lakshay Jethi with help and editing by Timothy G. Mack and Patanjali Kambhampati.

Chapter 4 is based on the article "The effect of Exciton-Delocalizing Thiols on Intrinsic Dual Emitting Semiconductor Nanocrystals", published in journal "ChemPhysChem" in 2016. This chapter demonstrates the influence of thiol ligands on the relative PL intensities of the core and surface emission in NC. The materials were synthesized by Lakshay Jethi and Timothy Mack. The linear spectroscopy and low temperature cryo-PL data was acquired by Lakshay Jethi with assistance from Sebastian Drake. The TCSPC measurement were performed by Lakshay Jethi and Timothy G. Mack. The modelling, DFT calculations and XPS experiment were performed by Timothy G. Mack. The data was analyzed by Lakshay Jethi. The manuscript was written by Lakshay Jethi and Timothy G. Mack with help and editing by Michael M. Krause, Tobias Kipp and Patanjali Kambhampati.

Chapter 5 uses the NCs in nanothermometry applications. It is based on the article "Towards Ratiometric Nanothermometry via Intrinsic Dual Emission from Semiconductor Nanocrystals", published in "Journal of Physical Chemistry Letters" in 2015. The chapter details ratiometric temperature sensing using intrinsic dual emission from CdSe NCs over a broad temperature range. The materials were synthesized by Michael M. Krause and Lakshay Jethi. The linear

spectroscopy and low temperature cryo-PL data was acquired by Lakshay Jethi. The data was analyzed by Lakshay Jethi. The manuscript was written by Lakshay Jethi and Patanjali Kambhampati with help and editing by Michael M. Krause.

LIST OF ABBREVIATIONS

ADMT	Adamantanethiol
CIE	Commission internationale de l'éclairage
Cryo-PL	Cryogenic Photoluminescence
DDT	Dodecanethiol
DFT	Density Functional Theory
ET	Electron transfer
FWHM	Full width at half maxima
GS	Ground State
HDA	Hexadecylphosphonic acid
HOMO	Highest occupied molecular orbital
LCD	Liquid Crystal Display
LED	Light Emitting Diode
LO	Longitudinal optical
LUMO	Lowest unoccupied molecular orbital
MBE	Molecular beam epitaxy
MeAc	Methyl Acetate
MeOH	Methanol
NC	Nanocrystal
PADT	10-(10-phenylanthrace-9-yl)-decane-1-thiol
PhS	Thiophenol
PL	Photoluminescence
PLMA	Poly(lauryl)methacrylate
QD	Quantum dot
QDTV	Quantum Dots Television
QY	Quantum Yield
RGB	Red, Green, Blue
RoHS	Restriction of Hazardous Substances
TCSPC	Time Correlated Single Photon Counting
TDPA	Tetradecylphosphonic acid
TEM	Transmission electron microscopy
ТОР	Trioctylphosphine
ТОРО	Trioctylphosphine oxide
TV	Television
UV	Ultra-Violet
XPS	X-Ray photoelectron spectroscopy

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I am thankful to Tim Mack for being the best colleague anyone could have. His intellectual curiosity and collaborative nature is commendable. It was so much fun to work with him in the lab. From broken flasks and overflowing waste bottles to making bright dots and trying new stuff, we had our share of lab moments. I am grateful to him for all his support in writing and editing of manuscripts and this thesis. Thanks for being a great friend!

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PhD studies are a significant (and long) time. The work environment and day to day contribution of everyone around you has a great impact. Special thanks to Hélène Seiler for being a motivating friend and chatting about science, life and food. I thank all the former members of the group, Jonathan Mooney, Jonathan Saari, Brenna Walsh, Pooja Tyagi for welcoming and introducing me to "Kambham-Life". I am grateful to all my colleagues Colin Sonnichsen, Patrick Brosseau, Harry Baker, Samuel Palato to convert this journey into a "Kambhamparty". Their comments and feedback throughout my PhD studies were helpful. I thank and wish the best to the new members, Dallas Strandell and Gabriela Romero Esquivel for taking over and bringing new ideas and direction to the materials group. I thank the visiting researcher, Tobias Kipp for his feedback and scientific discussions. I would also like to thank our office-mates from the Siwick Group, Martin Otto, Laurent de Cotret and Mark Stern for providing a pleasant environment to work.

I acknowledge the yearly feed-back from members of my PhD review committee, Bradley Siwick and Mark Andrews, which was valuable and helped me judge my progress. I would also like to thank Chantal Marotte for helping me with all the administrative and management work at the department. A special mention goes to the doctors and nurses at the Royal Victoria Hospital for my treatment!

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CHAPTER 1

Colloidal Semiconductor NCs

1.1 Introduction

In the present scenario where the entire world is technology and data driven, the fabrication and consumption of ever newer, smaller and quicker smart-gadgets is increasing. The demand of unabated miniaturization has reached new limits. Smaller sized structures in the range of nanometers are governed rather by "atomistic" physical laws than the bulk properties of the functional materials currently used in modern devices. Every aspect of our lives is becoming ever more digital with nanotechnology being used for innovations in engineering, medical devices, imaging, computing and many more¹⁻⁴. As these devices are made of thinner and thinner layers of material, interface and surface effects make it difficult for further miniaturization. At the same time energy losses increase as the surface to volume ratio is altered. A great variety of nanostructured materials can be used for miniaturization of such devices. Promising materials like semiconductor nanocrystals (NCs) and more recent "perovskites" can be exploited in the nanoscale regime to have better applications to outperform the current technologies.⁵⁻⁶

The emergence of many commercial applications of NCs over the past years has been very motivating.⁷⁻⁸ The primary focus of this research when I started my doctoral studies was to learn about nanoscale materials to be used in applications to create energy efficient and low power consuming devices. The direction of this research is aimed at studying optical properties of small colloidal semiconductor NCs to understand the tunability of the surface properties based on temperature, size as well as capping ligands.

Semiconductor NCs have small dimensions that consist of a limited number of atoms. They have properties intermediate between molecular and bulk forms of matter. These systems have been used in a multitude of applications over the past decade. As catalysts to make hydrocarbon from carbon dioxide⁹, to improve solar cells¹⁰⁻¹³, to treat antibiotic resistant infections¹⁴, to make memory chips using magnetic NCs in spintronic semiconductor devices. Colloidal NCs can also be used for producing images of cancer tumors. Currently this is used in lab animals to evaluate the performance of cancer treatments.¹⁵

The electronic and optical properties of NCs are closely related to the shape and size of the individual crystal.¹⁶⁻¹⁷ By controlling different conditions like precursor, ligand concentrations, time and temperature of reaction, NCs with different properties can be synthesized. Depending on the materials used such as Cadmium Selenide (CdSe), Cadmium Sulphide (CdS), Cadmium Telluride (CdTe), Indium Arsenide (InAs), Lead Sulphide (PbS), Zinc Selenide (ZnSe) etc.,

the emission wavelength can be placed over the spectrum ranging from UV to Infrared¹⁸. (Figure 1.1)



Figure 1.1 Semiconductor NC materials scaled as a function of their emission wavelength superimposed over the spectrum. Adapted with permission from reference 8. Copyright © 2018 American Chemical Society

The NCs were discovered in 1981 by Alexey I Ekimov¹⁹ in a glass matrix. Later, Louis E Brus²⁰⁻²¹ discovered the colloidal semiconductor NCs and the term "Quantum Dot" (QD) was first used in literature²². Since then the researchers have tried to use QDs in some form or the other to improve on existing technologies. Recent analysis of the global QD market suggests that it is expected to grow tremendously in future. QD market segments currently include healthcare, medical equipment, LED lighting, optoelectronics, displays, telecom, flash memory, lasers, quantum computing and sensors²³. According to market research reports, the industry that was worth around \$300 million in 2014, is expected to be worth over \$8 billion by 2023²³. With companies like Apple, SONY, Samsung and LG investing in R&D of QD based devices along with various QD manufactures like Nanoco Group, Nanosys and Quantum Materials, the industrial commercialization of QDs has already begun (Figure 1.2). SONY introduced the first Triluminos TV with QDs back in January 2013 in the W90 model. The tiny dots have since been implemented in the Amazon Kindle Fire tablet and Asus laptop displays. Recently, Samsung unveiled QDTVs with inorganic QDs which are cadmium-free to address environment toxicity related issues.



Figure 1.2 The growing quantum dot industry with major companies involved in R&D and development of consumer devices²⁴⁻²⁶

The current commercial applications of semiconductor nanocrystals have grown rapidly. Table 1.1 summarizes some of the applications along with the manufacturers. The key markets that use high volume of industrially produced NCs are display devices, energy and biomedical.

Market	Application	Manufacturers
Display	Color enhancing films	Evident Technologies Nanoco Nanosys, Inc. N-N Labs Quantum Materials Corp LG Display Samsung Sony
Energy	Solar cell films Battery additives Thermoelectric superlattice	Dupont Phillips Revolution Lighting Technologies Sharp Corporation Evident Technologies Nanosys Inc. Pacific Light Technologies StoreDot Quantum Materials Corporation Kopin Corporation KRI, Inc. Nanoco Technologies Ltd Natcore Technologies Ltd Natcore Technologies Ocean NanoTech Solterra Renewable Technologies, Inc
Biomedical	Contrast agents In-vivo imaging Tumor cell markers Immunoassays Molecular imaging Fluorescent probes Drug delivery and tags Toxin detection	Antibodies Incorporated Attonuclei Cromoz Inc. DiagNano Evident Technologies Helicos BioSciences Corporation Invitrogen Corporation Luminex Corporation Nanoco Group plc Quantum Materials Corp.
Security	Anti-counterfeiting inks	Nanoco QDLight Quantum Materials Corporation Voxtel
Sensors	Chemical Sensors Gas Sensors	Nanosys StoreDot InVisage 3M

Table 1. 1 Semiconductor NC market and applications

1.2 Quantum Size Effect in Semiconductor NCs

As things are rapidly shrinking in modern day semiconductor devices, it has always been a fascinating area of research to see how electronic properties of nanocrystals change with size. Optical spectroscopic experiments have enabled us to learn more about such systems over the last couple of decades. The atom like behavior in small sized semiconductors is attributed to *quantum-size effect*²⁷⁻²⁹, where the bulk bands of the semiconductor become quantized. Semiconductors can absorb photons causing an electron to transition from valance band to conduction band. This transition leads to the formations of an exciton (bound electron-hole pair)³⁰⁻³¹. The carriers are then confined by the walls of the material, if the size of the semiconductor is comparable to the exciton length.³²

In CdSe NCs this effect is so pronounced that it makes them one of the most reliable system to study the underlying phenomenon. The NC can be understood as a typical textbook 1D particle in a box approximation. The charge carrier is confined and can only move in one dimension. This forms a potential well in one dimension in the conduction and valance bands. The bands are therefore quantized into electron and hole levels and the particle can only exhibit a series of discreet transitions between these quantized states. The electron and hole energy levels are sensitive to the extent of confinement, thereby making the optical properties strongly depended on the size of the particle. To compare the size of the exciton to the dimension of the confining particle, Bohr radius is used as a suitable length scale. The Bohr radius of an exciton is given by equation 1.1

$$a_{exc} = \varepsilon \frac{m}{m^*} a_0 \tag{1.1}$$

where *m* is the mass of an electron at rest, m^* is the mass of the exciton, ε is the material specific dielectric constant and a_0 is the radius of the hydrogen atom. In the case of NCs, equation 1.1 can be used to calculate Bohr radii for electron (a_e) , hole (a_h) , and the electron-hole pair i.e. exciton (a_{exc}) . Considering three different limits, different confinement regimes can be defined for a NC with radius (a)

$a < a_e, a_h, a_{exc}$	 strong confinement regime
$a_e, a_h < a < a_{exc}$	– weak confinement regime
$a_h < a < a_e, a_{exc}$	– intermediate confinement regime

CdSe NCs can either be in strong or intermediate confinement regimes as the Bohr radius of the exciton, a_{exc} in CdSe is ~6 nm³³



Figure 1.3 Schematic representation of quantum confinement effect showing the bandgap of NCs increasing with decreasing size.³⁴ Adapted with permission from reference 10. Copyright © The Author(s) 2016. Open Access under the terms of the Creative Commons Attribution 4.0 International License (http://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/)

1.3 Semiconductor NC as "Particle in a Box"

The simplest form of the particle in a box model³³ considers a one-dimensional system. In such a system, the particle may only move backwards and forwards along a straight line with impenetrable barriers at either end. In the case of NCs, it is more like "a particle in a sphere". This model describes the exciton as a particle with mass m_0 and the NC as a spherical potential well of radius *a*. The walls of the spherical potential well may be visualized as regions of space with an infinitely large potential energy. The inside has a constant, zero potential energy. This means that no forces act upon the particle inside and it can move freely in that region. However, infinitely large forces repel the particle if it touches the walls, preventing it from escaping. The potential energy in this model is given as

$$V(r) = \begin{cases} 0, & 0 < r \le a \\ \\ \infty, & r > a \end{cases}$$
(1.2)

The wavefunction can be found by solving the Schrödinger equation for the system

$$\Phi_{n,l,m}(r,\theta,\phi) = C \frac{j_l(k_{n,l}r) Y_l^m(\theta,\phi)}{r}$$
(1.3)
where $Y_l^m(\theta, \phi)$ is a spherical harmonic, $j_l(k_{n,l}r)$ is the *l*th order spherical Bessel function, $k_{n,l} = \alpha_{n,l}/a$, which is the nth zero of j_l . The energy of the particle is given as:

$$E_{n,l} = \frac{\hbar^2 k_{n,l}^2}{2m_0} = \frac{\hbar^2 \alpha_{n,l}^2}{2m_0 a^2}$$
(1.4)

Where, energy is inversely proportional to the a^2 , therefore dependent on the size of the particle. The above equation does not consider the fact that the NCs are filled with atoms and assumes it to be a hollow sphere. The "effective mass approximation" model can be used to estimate the bulk conduction and valance bands as isotropic bands with simple parabolic forms. Within this approximation, individual atoms in NC lattice can be ignored and electron and holes are treated as free particles with different effective masses in parabolic energy bands.

The conduction and valance band energies are approximated as:

$$E_{k}^{c} = \frac{\hbar^{2}k^{2}}{2m_{eff}^{c}} + E_{g}$$
(1.5)

$$E_k^{\nu} = -\frac{\hbar^2 k^2}{2m_{eff}^{\nu}}$$
(1.6)

where m_{eff} is the effective mass of the particle and E_g is the semiconductor bandgap.

Further, to account for the fact that in NCs the exciton is confined in a finite sphere, "envelop approximation function" is employed. This allows for the carrier wavefunction to be written in terms of Bloch functions, u_{nk} , used for particles in a periodic environment like a bulk semiconductor. Using this approximation, the wavefunction of the particle is given as

$$\Psi_{sp}(\vec{r}) = u_{n0}(\vec{r}) \sum_{k} C_{nk} \exp(i\vec{k} \cdot \vec{r}) = u_{n0}(\vec{r}) f_{sp}(\vec{r})$$
(1.7)

with a weak crystal momentum (k) dependence of u_{nk} . $f_{sp}(\vec{r})$ is the single particle envelope function. The periodic Bloch functions can be approximated as a sum of atomic wavefunctions $\varphi_{n,k}$, where n can either stand for valance or conduction band, and can be written as

$$u_{n0}(\vec{r}) \approx \sum_{i} C_{n,l} \varphi_{n,k}(\vec{r} - \vec{r}_{i})$$
 (1.8)

As shown in Eq. 1.4, the particle energy is inversely proportional to a^2 , and the electron-hole Coulomb interaction is 1/a in the limit of small radius NCs, electron and hole can be treated as independent particles since in strongly confined NCs (i.e. small sized) the quadratic term will dominate. The Coulomb interaction can be added as a first-order correction to the excitonic energy. This approximation is called the "the strong confinement approximation"³⁵. Finally, the excitonic wavefunction is written as

$$\Psi_{exc}(\vec{r}_{e},\vec{r}_{h}) = \Psi_{e}(\vec{r}_{e})\Psi_{h}(\vec{r}_{h}) = u_{c}f_{e}(\vec{r}_{e})u_{v}f_{h}(\vec{r}_{h})$$
$$= C\left(u_{c}\frac{j_{L_{e}}(k_{n_{e}L_{e}},r_{e})Y_{L_{e}}^{m_{e}}}{r_{e}}\right)\left(u_{v}\frac{j_{L_{h}}(k_{n_{h}L_{h}},r_{h})Y_{L_{h}}^{m_{h}}}{r_{h}}\right)$$
(1.9)

Therefore, the energy levels are given as

$$E_{exc}(n_e L_e n_h L_h) = E_g + \frac{\hbar^2}{2a^2} \left(\frac{\varphi_{n_e L_e}^2}{m_{eff}^c} + \frac{\varphi_{n_h L_h}^2}{m_{eff}^v} \right) - E_c$$
(1.10)

where E_c is the Coulomb interaction correction term and $n_e L_e n_h L_h$ (n=0,1,2...; L=s, p, d...) are the quantum numbers labelling different states.

1.4 Composition of Semiconductor NCs

As described, the bandgap of different NCs is tunable over different wavelengths based on size and depending on the exciton Bohr radius. Another approach to control the properties of semiconductor NCs is by making NC heterostructures where two or more different NCs are joined together³⁶. This approach can alter the spatial localization of the charge carriers by changing the band offsets of the different materials combined together.^{34, 36} Based on the charge carrier localization, different types of hetero-NCs can be synthesized. NCs systems like CdSe/ZnS, InP/ZnS (core/shell), where both charge carriers are localized in the same region are referred to as type-I heterostructures. A reverse type-I system can also be formed with a narrow bandgap material shell overgrown onto the core with a wider bandgap. The charge carriers are partially delocalized in shell and the shell's thickness can be altered to tune the emission wavelength (for example CdS/HgS³⁷, CdS/CdSe³⁸, ZnSe/CdSe³⁹).

Contrary to that, in type-II heterostructures, the charge carriers are spatially separated in different materials i.e. the electron and hole wavefunctions are positioned in different regions. Examples of such systems are CdSe/ZnTe, CdSe/CdTe heterostructures. Another type of hetero-NC is the quasi-type-II heterostructure like CdSe/CdS or ZnSe/CdSe where one charge carrier is delocalized over the entire NC while the other is localized in one region. Such hetero-NCs allow for a greater control of NC properties like quantum yield,

stability as well as radiative lifetimes⁴⁰⁻⁴⁵ by modifying the electron-hole spatial overlap, based on size, shape and composition. This degree of tunability is advantageous in designing efficient light emitting and lasing devices using NCs^{46-⁴⁷. A variety of complex shell structures have been reported that enable dual emission from both core and shell materials⁴⁸⁻⁵⁰. Another example of dual emission is from the core and the "surface" of semiconductor NCs which is described in this thesis based on the prior work done by our group⁵¹.}



Figure 1.4Schematic of the energy level alignments and carrier localizations in type I, reverse-type I, type II, and quasi-type II core/shell NCs. Red and blue lines indicate electron and hole wave functions, respectively⁵²Adapted with permission from reference 27 Copyright © 2017 Korean Ceramic Society. Openaccess under the terms of the Creative Commons Attribution Non-Commercial License (<u>HTTP://CREATIVECOMMONS.ORG/LICENSES/BY-NC/3.0/</u>)

1.5 Surface of NCs

For a spherical particle with 1 nm radius, approximately 67% of the total atoms are surface atom. With such a majority of atoms on the surface, it is apparent that surface effects will dominate in governing many properties of small sized NCs. The most obvious effect in nanoscale materials is the increase in surface to volume ratio as the size is decreased. The atoms on the surface of NCs have high energies and dangling bonds thereby making them more reactive compared to their bulk forms. Moreover, properties like solubility, dispersity and catalytic activity are governed by the surface of NCs^{36, 53}.

The optoelectronic properties of NCs are also affected by the large surface-volume ratio. The unshared atomic orbitals of the surface atoms are believed to give rise to localized energy levels within the bandgap of the NCs. These energy levels are known as "trap states"⁵⁴⁻⁵⁵ and are considered to arise from uncontrollable defects. The carriers can relax into these states either radiatively (known as trap state PL or surface PL) or non-radiatively. The trap-PL is often seen as a red shifted broad emission which generally is unfavorable for narrow bandwidth applications of NCs. Therefore, it is often eliminated by growing shells or by using ligands that lower the energy of surface atoms by forming stronger bonds⁵⁶. This thesis focuses on small CdSe NCs with surface PL to exploit it for white light generation (section 1.7). Studies from prior work in our group suggest that the surface PL can be controlled and the electronic structure of such "surface states".

can be understood in terms of simple electron transfer theory⁵⁷⁻⁵⁹. This is discussed in greater detail in following sections of the thesis.

The surface of colloidal NCs are usually capped with 'ligands'. Ligands serve to passivate the surface of the QDs, reducing trap states and preventing colloidal aggregation, as well as determining which solvents the QDs can be suspended in⁶⁰. Additionally, they also directly impact the optical properties of the quantum dots⁶¹⁻⁶². Some ligands also enhance the photoluminescence properties of NC significantly⁶³. Ligands on the surface of NCs can also be swapped through ligand exchange procedures⁶⁴ (see chapter 2). Ligand chemistry therefore, can further alter the NC properties tailored for specific applications^{51, 59, 65}. The ligand distribution and structure of NC surface is a continuing area of research.

A wide variety of organic molecules can act as ligands for NCs. While the bulk of the work in the field focuses on organic ligands, inorganic ligands are also being researched.⁶⁶ The interactions of ligands with the surfaces of quantum dots are dependent on both ligand and quantum dot surface structure. Ligands can bind to the surface of NC in various geometries. Every geometry has an associated adsorption constant⁶⁷, which eventually leads to varied electronic properties of NCs⁶⁸⁻⁶⁹

Based on the bond classification method of MLH green⁷⁰, Owen group⁷¹⁻⁷² has proposed a model for ligand passivation to categorize the interaction of ligands with NC surface (Figure 1.5). The ligands can be divided into three categories: L-

type, X-type and Z-type. L-type ligands are two-electron donors (Lewis bases) and form dative covalent bonds with neutral surface metal sites. Amines, thiols, and phosphines are common L-type ligands. Anionic, single electron donors are categorized as X-type ligands. They form ionic or covalent bonds with cationic surface metal sites. X-type ligands include carboxylates, thiolates, phosphonates, and halides. Lastly, Z-type ligands are two-electron acceptors (Lewis acids) which bind to neutral chalcogenide surface sites. Z-type ligands include lead chloride and cadmium stearate.



Figure 1.5 Nanocrystal ligand binding motifs according to the covalent bond classification method⁷¹ Reprinted with permission from reference 42. Copyright © 2013 American Chemical Society

The PL quantum yield is also strongly dependent on the nature of ligands used. The traditional synthesis with TOPO/TOP mixtures had lower QYs (<10%) compared to ligands using phosphonic acids, like HDA/TOPO/TOP which can yield QYs as high has 85%⁷³. The ligand can also alter the PL spectra of the NC after a ligand exchange procedure is performed (see chapter 2). Depending on the type of ligand used, the PL can be quenched or enhanced dramatically. Alkyl amines are known to enhance the PL QYs of NC by an order of magnitude^{61, 74-⁷⁵.On the other hand, PL QY of NCs are reported to decrease by use of thiol ligands⁷⁶}

1.6 Linear Spectroscopy of CdSe Nanocrystals

Absorption of a photon by the NC occurs if its energy exceeds the band gap. As described earlier, the quantum confinement effect in decreasing particle size results in a blue-shift (hypsochromic) of the absorption onset. The exitonic peak is observed as a sharp absorption feature. It is the lowest excited state with the largest oscillator strength. The width and position of this feature depends on the particle size distribution and band gap respectively. Polydisperse samples typically exhibit only a shoulder in the absorption spectrum at the position of the excitonic transition. Higher energy excited state absorption can also be observed at shorter wavelengths. The larger the number of such spectral features and the more distinctly they are resolved in the absorption spectrum, the smaller is the size dispersion of the sample⁷⁷. (Figure 1.6)



Figure 1.6 Absorption and PL spectra of CdSe NC

Photoluminescence is the property of a semiconductor to absorb photons with an energy superior to its band gap and fluoresce. After the charge carrier is relaxed via phonons to the lowest excited state, semiconductors emit light of a longer wavelength. The time interval is called the fluorescence lifetime. The emitted photons have an energy corresponding to the band gap of the NCs and for this reason the emission color can be tuned by changing the particle size (Figure 1.7). The usual FWHM for CdSe NC samples at room temperature is in the range 20-40nm with a Stokes shift of about 10-20 nm⁷⁸



Figure 1.7 Tunability of emission wavelength of NCs based on the size⁷⁹

1.7 White light Emission from Semiconductor NCs

Over the last decade, many advances have been made in improving and understanding semiconductor NCs for white light applications. The use of white light emitting devices has grown rapidly due to their high efficiencies and longer lifetimes. The most traditional and common way of generating white light is to use a yellow phosphor on top of blue Gallium Nitride (GaN) LEDs⁸⁰. However, other methods using photoluminescent as well as electroluminescent properties of semiconductor NCs have recently gained attention of researchers. Like phosphors, NCs too can be adopted as down-conversion materials that convert the shorter blue wavelength to longer wavelengths. For such down conversion, the NCs are usually dispersed in a polymer matrix. CdSe/ZnS core/shell NCs dispersed in Poly(lauryl)methacrylate (PLMA) matrix on top of GaN blue source is one such example⁸⁰. Another approach uses multi-shell CdSe/ZnS/CdSZnS for green and CdSe/CdS/ZnS/CdSZnS for red color convertors for high quantum yields.⁸¹ White light emitting compounds can also be synthesized by grafting blue-emission fluorescent molecule of the anthracene derivative (10-(10-phenylanthrace-9-yl)-decane-1-thiol, PADT) onto yellow emitting CdSe/ZnS NCs⁸²

An alternative approach to generate white light is to mix two or three different color emitting NCs in a layered structure. This was demonstrated by Anikeeva *et al*, in a hybrid organic/inorganic structure utilising red, blue and green (RGB) emitting NCs.⁸³ Such layered structures along with multistep synthesis of NCs and fluorescent molecules are complicated. Moreover, they are susceptible to efficiency losses due to self absorption⁸⁴.

A more recent and facile method to generate white light has been shown by Sheng et al.⁸⁵ where a single pot dual-color NCs (green and red) synthesis have been reported using thermal pyrolyzed chemical synthesis. This method doesn't require multi-step synthesis procedures thereby making the process simpler, but there still remains the question of aging and stability of different type of NCs (red and green) multiplexed together.

Another different method to generate white light is to synthesize very small NCs. Such small NCs were first synthesized in early 2000s. Soloviev et al reported a molecular cluster of phosphine capped CdSe molecular cluster consisting of 32 cadmium atoms.⁸⁶ The idea was based on the synthesis chalcogenide molecular cluster by Choy et al and Herron et al⁸⁷⁻⁸⁸. An alternative approach to make NCs with 1.6 nm diameter was shown by Landes et al by reducing the reaction temperature to slow down the reaction kinetics.⁸⁹ These synthesis used highly reactive and toxic dimethyl cadmium or cadmium chloride as precursors. Later, Peng et al and reported the use of cadmium oxide, cadmium oleate and cadmium stearate in combination with alkyl phosphonic acids to synthesize high quality NCs⁹⁰⁻⁹³. These cheaper and practical synthesis procedures allowed for the observation of nanocrystal growth and nucleation at slower rates.⁹⁴ Due to their reproducibility in absorption peak at 285 and 349 nm^{91, 95} and thermodynamically stable cluster of exact number of atoms, these NC were termed as "magic sized nanocrystals". Since then various methods have been developed to synthesize magic sized nanocluster using fatty acids, phosphonic acid as well as phosphinic acids.⁹⁶⁻¹⁰¹ A list of common CdSe magic sized nanocrystals based on highest energy absorption peaks and ligands was detailed by Harrel et al⁹⁵ in tabular form. Their data suggested that either different ligands are responsible for energetically favouring specific number of atoms of cadmium and selenium to form magic sized NCs or the energy of the bandgap is dependent on the ligands.

In contrast, "ultra-small nanocrystals" with characteristic white light emission were observed by Bowers et al,¹⁰². They showed synthesis of 1.5 nm CdSe nanocrystals by rapidly stopping the growth using a butanol injection¹⁰². As reported, these ultra-small nanocrystals were not magic sized. Unlike magicsized NC growth where discreet sizes are observed (heterogeneous)^{96, 103-104}, ultra-small NC exhibit continuous redshift during the process (homogeneous)¹⁰⁵. Moreover, the ultra-small NCs are had broader FWHM compared to narrow FWHM in magic sized NCs.⁹⁵

This thesis focuses on such ultra-small NCs show dual band emission. They are known to emit light that is broadened and redshifted (trap PL/surface PL) with respect to the well-known emission from the excitonic "core". As mentioned above in section 1.5, this broad emission is conventionally seen as a problem to mitigate as it affects the PL QY of the NCs. However, these NCs can potentially be used to generate white light from a single emitter without the need of multiplexing or down conversion.

As described in section 1.2 and 1.5, the optical properties in NC arise form the quantum confinement effect. However, surface of the small NCs act as a finite potential barrier which results in wavefunction leakage.¹⁰⁶ On the surface of such NCs their lies the mid-bandgap trap states⁵⁴⁻⁵⁵ known to arise from

uncontrolled defect states. When a leaked charged carrier is trapped on such a site, it relaxed either radiatively or non radiatively¹⁰⁷⁻¹⁰⁸ thereby, altering the PL quantum yield of the NCs. Based upon this, the understanding and control of NC properties is highly desirable to obtain high quantum yields. This is the reason that researchers have been using methods like shelling the NCs with higher bandgap materials e.g. ZnS to discard this "surface" emission. The shell limits non-radiative traps to core defects and the boundary between the two semiconductors¹⁰⁹. Hence, current applications based on NCs employ the spectrally narrow emission from the core exciton¹¹⁰⁻¹¹⁴.

Spectrally, this surface emission gives rise to what we see as white light emission (Figure 1.8). Control of surface emission can provide small NCs as potential candidates in "white" light emission for display, lighting, sensing and variety a of other applications. The surface emission of CdSe NCs have recently been exploited to develop white light sources for displays, lighting, and even optical thermometry.^{51, 59, 115-116}



Figure 1.8 White light emission spectra. White light emitting CdSe NCs compared to regular large sized NCs (inset)

1.8 Semiclassical Marcus-Jortner Electron Transfer Theory – Prior work

The above discussed broad and red-shifted spectral property of NCs is supposed to arise from the surface trap states that have a large energy distribution within the band gap. Initially, it was rationalized by the distribution of trap states^{54, 117} (Figure 1.9 a-b). This model suggested an irreversible relaxation from the core excitonic state to the trap states with negligible temperature dependence since the redshift is an order of magnitude larger (>10k_BT) than the available thermal energy^{54, 117-118}. Further, the surface emission does not red-shift with decreasing temperature which shows that the trap states are not randomly distributed. Therefore, this theory fails at describing the temperature dependence of the surface PL. In order to understand the temperature dependence, the configuration coordinate approach with an energy barrier for the carriers (ΔG^*) can be used to describe the thermodynamics of core and surface populations. This approach was used by Jones et al¹¹⁹ with the classical Marcus electron transfer theory to explain the temperature dependent PL lifetimes. In this model the surface state must lie within k_BT below the core state and the energy barrier must be lower than the free energy (ΔG) (figure 1.9 c-d). As the temperature is lowered, the decrease in the thermal energy favorably populates the surface state only apply when the surface can only be displaced to a certain extent on the classical polarization coordinate. Therefore, this approach does not account for the red-shift and broadening of the surface emission.



Figure 1.9 Three different models to explain temperature dependent PL: (a) The classical deep trap model does not account for the different functional form of temperature dependent core and surface intensity changes. (c) The classical Marcus model does not explain breadth nor position of the surface emission. (e) Semi-classical Marcus–Jortner ET model explains temperature dependent PL changes and spectral features of NCs. (b), (d), and (f) are the corresponding generic temperature dependent PL spectra. Reprinted with permission from reference 91. Copyright © 2013 American Physical Society.

Our group has previously shown that this surface PL arises from surface states of the NC that are electronically coupled to the core excitonic states^{57, 59, 120-121} using the Marcus-Jortner Semiclassical Electron Transfer theory in a configuration coordinate scheme. This scheme can be described using the following Marcus-Jortner ET rate equation:

$$\frac{1}{\tau_{ET(forward)}} = \frac{1}{\tau_f} \left(\frac{\pi}{\hbar^2 \lambda_m k_b T}\right)^{\frac{1}{2}} e^{-S} \times \sum_n \frac{S^n}{n!} e^{\frac{-(\Delta G + \lambda_m + n\hbar\omega)^2}{4\lambda_m k_b T}}$$
(1.11)

Where ΔG represents the energy difference between the 1S and the surface state, λ_m represents the medium reorganization energy and the Huang-Rhys coupling parameter, S represents the internal quantum mode (see Figure 1.10).



Figure 1. 10 Configuration coordinate scheme showing Marcus–Jortner electron transfer theory assuming a steady-state three-state model

Figure 1.9 e-f schematically illustrates the model where a core excitonic state (1S) is coupled to a surface state. In such a model, the ligand-bath interactions are governed by the classical mode while the quantum mode corresponds to the longitudinal optical LO phonon or a ligand vibration. The quantum mode(s) allows the tunneling through the potential barrier which determines the nature of electron transfer at low temperatures ⁵⁷⁻⁵⁸. Classically, the free energy (Δ G) difference dictates the thermodynamics of the population equilibration between the core and the surface states.¹²¹ The strongly coupled LO phonons to the surface state produce the characteristic broadened and redshifted surface band originating from Franck-Condon progressions.⁵⁷



Figure 1.11 Thermodynamic control of PL spectra and color rendering capacity CIE diagrams for different temperatures. The arrows mark the change of color from cryogenic to room temperature. (b) The color of butylamine passivated NCs at room temperature in the blue/ violet color region in addition to the color trajectory. Reprinted with permission from reference 36 Copyright © 2013 American Chemical Society

This model can rationalise the charge carrier transfer between the core and the surface states in a simple manner. Further, this model has been used by our group to explain different radiative trends for NCs passivated with different ligands as well. The temperature dependent data was fitted to the model for two different types of ligands (TOP and N-Butylamine). The results showed that free energy change of the surface state after the ligand exchange and the ratio of surface to core PL can be controlled with temperature.⁵⁹ Figure 1.11 shows the thermodynamic control of white light and PL spectra by altering the core PL to surface PL ratio for different ligand passivation and temperature.

This thesis further discusses the applications of the above described model to understand the behaviour of small NCs based on other ligand types (thiols¹²²), size¹²³ and temperature dependent⁵¹ properties in following chapters. The Marcus-Jortner model described above is based on experimental observations. Details like chemical specificity, surface trapping of charged carriers, surface passivation and structure cannot be described without the aid of high level computational atomistic theories¹²⁴.

1.9 Conclusion

To conclude, it can be said that the semiconductor NCs are extraordinary materials which are already being used in various commercial applications. Different combinations and compositions can result in improving several properties of NCs. Increasing need of white light producing materials is growing, where NCs seem to produce promising results. This material has seen incredible advances over decades and is still being studied to understand the surface structure and properties. The temperature dependent spectroscopic properties of NCs can be understood by a simple model described previously by our group. The following chapters will discuss the size, temperature and ligand dependence of small NCs in detail based on the experimental work performed for this thesis.

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CHAPTER 2

Synthesis and characterization of semiconductor nanocrystals approaching the molecular cluster limit

This chapter was partially adapted from the manuscript, "Synthesis and characterization of semiconductor nanocrystals approaching the molecular cluster limit", Submitted

Semiconductor nanocrystals (NC) can be controlled in size and emission to span the limit from larger quantum dots to smaller molecular clusters. The synthesis and characterization of larger NCs has been well established but the characterization of small NCs approaching the molecular limit is still a challenge. This chapter describes the synthesis of small CdSe NCs approaching the molecular cluster regime and discusses the quality and properties of small NCs using XPS, Raman spectroscopy, TEM and UV spectroscopy. These methods reveal the presence of small NC with stronger line broadening and pronounced surface properties which are discussed in following chapters. Further, this segment of the thesis details the other experimental techniques used such as ligand exchange process, cryo-PL measurements and TCSPC lifetime measurements.

2.1 Introduction

The unique size and shape dependent spectroscopic properties of colloidal NC makes them one of the most broadly studied systems. After being studied for various applications in sensing¹⁻², imaging³⁻⁴, biomedicine⁵⁻⁶ as well as catalysis⁷ over the past two decades, vast efforts have been done to design and synthesis nanocrystals with desired properties for next generation applications⁸⁻¹². A variety of synthetic approaches have been employed for colloidal NCs such as hot-injection¹³⁻¹⁵, non-injection¹⁶⁻¹⁷, aqueous synthesis¹⁸, biosynthesis¹⁹ and even using olive oil²⁰ and urine!²¹

The main benefit of using colloidal semiconductor NCs is that they are costeffective with a good size distribution and shape specificity²². Moreover, colloidal synthesis allows for NC properties to be altered through ligand functional group modification²³⁻²⁴, but there remain many challenges for characterization to study the structural properties of small NCs.

In contrast to widely developed synthesis of NCs in the quantum dot regime, the synthesis and characterization for NCs approaching the molecular cluster regime is less developed. The size of the standard NCs can range from 2-10 nm in diameter. The physical characterization of NCs with diameters less than 2 nm is challenging. The contrast in TEM is weak and broad spectral features draw in the question of sample quality. The ability to synthesize and characterize such small NCs reproducibly can further enable us to understand the surface properties. This can also allow for exploiting the surface of NC to be used for various applications such as water splitting and catalysis more efficiently²⁵⁻²⁶.

As discussed in chapter one, the three regimes of size-dependant quantum confinement identified by Efros are the weak (R>>R_B), intermediate (R~R_B) and strong confinement (R<<R_B)²⁷ where R is the radius of NC and R_B is the bulk excitonic Bohr radius. The regime of nanocrystals largely explored involves the transition from the bulk, to the quantum dot (QD) regime. A similar understanding of the transition from the QD regime to the molecular cluster regime is essential for better understanding the properties of smaller NCs. This chapter discusses the synthesis of small NC in the molecular cluster regime (sub 2 nm radii)²⁸ to assess their quality. The size of the NCs were controlled to be under 2 nm in radius. As the size is reduced, the absorption peaks shift to larger energies.

Figure 2.1 shows this transition using standard empirical sizing curve for CdSe as described by Yu et al²⁹. The quality of such NCs is evaluated here based on UV-Visible spectroscopy along with X-Ray photoelectron spectroscopy (XPS), Raman spectroscopy and Transmission electron microscopy (TEM). Our findings

show that the synthesized NCs are on par with commercially available NCs with similar sizes. Moreover, it was found that the sample preparation steps are very crucial for each characterization technique and have been described in this article.



Figure 2. 1 a) Size dependence of CdSe NCs showing a large shift in absorption peaks in small NCs, b) size dependence of NC showing PL emission

2.2 Nanocrystal Synthesis

Colloidal CdSe NCs studies in this thesis were prepared with slight modifications following the hot-injection work of Peng and Peng¹⁴. Separate vials were prepared for injection solution and rinsing solution. Injection solution was made by dissolving 0.356 g of Se in 2 g of TOP in a glove box under argon. Another vial with 2g TOP was prepared for rinsing the sides of the flask. A three-necked round bottom flask with 0.523 g of CdO, 3.96 g of TOPO, and 0.211 g of TDPA was

evacuated and argon was introduced. While stirring the flask was heated to 310 °C, and the sides of the flask were rinsed down with ~2 g of TOP once the temperature was reached. The flask was let to recover the temperature back to 280 °C and the contents of injection solution (Se/TOP) were quickly introduced into the flask using a syringe (Figure 2.2). Se/TOP immediately gets thermally decomposed into supersaturated selenium monomers which are relieved by the creation of CdSe nuclei. As the monomer concentration reaches below the nucleation threshold, CdSe NC start forming.



Figure 2.2 Illustration showing synthesis and NC growth process

This process can be understood in terms of LaMer Model³⁰⁻³¹. In The reaction was cooled simultaneously by immersing the flask in a water bath. Once the reaction had cooled to about 80 °C, the reaction mixture was transferred to a centrifuge tube and was fractionally centrifuged with MeAc at 10000 rpm for 10 min to remove larger NCs. Centrifuge step was repeated and finally the NCs were dissolved in toluene. To remove excess cadmium from the NCs dispersed in toluene, either the NCs were centrifuged in toluene at 10000 rpm for 2 mins or filtered using a syringe filter. This removal of excess cadmium is crucial for sample preparation for various characterization techniques, especially for TEM. For size dependent studies in chapter 3 the reaction was cooled at different times (3s, 7s, 11s, 16s, 30s, 50s, 80s, 120s, 150s, 180s) to create NCs of different sizes.

2.3 Nanocrystal characterization and techniques

The spectral quality of the NCs synthesized were compared to commercially available (NNLABS 480) NCs with similar band edge emission. The photoluminescence and absorption spectra for synthesized NCs in comparison with commercially available similar sized NCs is shown in Figure 2.3. The absorption and PL spectra quality is analogous. The absorption peaks are well resolved and overlap, as well as the PL line-shapes are similar. The size of the synthesized small NCs determined using the empirical equations²⁹ is ~ 1.07 nm.

Our group has shown the spectral behavior of small nanocrystals in the molecular cluster regime.^{28, 32-33} The broadening of the PL line-shapes i.e. large FWHM values for smaller NCs has been observed which is discussed in greater detail in Chapter 3. Figure 2.3b shows that within the molecular cluster regime (radius <1.2 nm) the FWHM values are larger. This innate property is independent of the quality of the samples. In fact, the emission line-width of such NCs are dictated by their surface, where increased coupling to the ligands is observed.²⁸ Moreover, the FWHM of commercially available NCs compared to our sample are alike with values ranging from 140-180 meV.



Figure 2.3 a) Absorption and PL spectra of small NCs compared to commercially available NC of similar size. b) Size dependence of the FWHM for small NCs (sub 2nm) showing a large increase in the molecular cluster regime.

2.4 Ligand Exchange

The surface and properties of semiconductor NC can be modified by changing ligands surrounding it. Ligand exchange from phosphonic acid ligands (TDPA) to thiols for studies in Chapter 4 were performed using the following procedure. A three-neck round bottom flask with 3mL of prepared NCs was attached to Schlenk line to evaporate all toluene under vacuum for ligand exchange. 3mL/1g DDT/ADMT was injected and solution was constantly stirred and maintained at 80 °C/110 °C for 15 minutes to complete the ligand exchange process. The obtained NCs were then centrifuged with MeAc at 10000 rpm for 10 minutes. The supernatant was discarded, and the precipitate was suspended in toluene. Some of the ligands used for studies in this thesis are shown in Figure 2.4.



Figure 2.4 Structure of different ligands binding CdSe NCs.

2.5 Cryo-PL experiments

For low temperature PL measurements, polystyrene (1g) -NCs solution (1mL) in toluene (10mL) was prepared and drop cast in a petri-dish. The petri-dish was covered and films about 0.5 mm thickness were obtained after two days of drying. These films were mounted on a continuous flow liquid nitrogen cryostat (Janis STVP-100) under high vacuum. Sample temperature was monitored using Lakeshore temperature controller (Model 331). Photoluminescence spectra was acquired at various temperatures using a Spex Flouromax 2 spectrofluorometer.

2.6 Time Correlated Single Photon Counting (TCSPC)

TCSPC fluorescent lifetimes were measured using an Edinburgh mini-tau instrument. The samples were excited using a 405-nm diode laser and data was collected with the appropriate color filters and detection window. The data acquired was fitted by re-convolution with IRF (instrument response function) using blank solvent. The fit equation is given as:

$$Fit = B + \alpha_1 e^{(-\frac{t}{\tau_1})} + \alpha_2 e^{(-\frac{t}{\tau_2})} \dots$$
(2.1)

where B is a background parameter., τ_i is the decay time, and t is time. The decays were fit to multiple exponentials, which is a common procedure for NC PL lifetime measurements³⁴,³⁵ The numbers of exponentials are generally chosen

in order to obtain reduced χ^2 values around 1, indicating a good fit. The average lifetime was calculated using the following formula³⁶:

$$\tau_{av} = \frac{\sum_{i} \alpha_{i} \tau_{i}^{2}}{\sum_{j} \alpha_{j} \tau_{j}} = \frac{\alpha_{1} \tau_{1}^{2} + \alpha_{2} \tau_{2}^{2}}{\alpha_{1} \tau_{1} + \alpha_{2} \tau_{2}} \dots$$
(2.2)

2.7 Transmission electron microscopy (TEM)

The TEM measurements were performed on Jeol JEM-2100F analytical transmission electron microscope equipped with energy-selective X-ray spectrometer for chemical analysis. The samples were prepared by placing a drop of diluted NC solution on formvar coated Cu TEM grids for 45 seconds and eventually wiped off using KimWipe.

TEM of small NCs compared to a commercial CdSe NC with similar size (Figure 2.5). The NCs obtained using the proposed synthesis are well dispersed with uniform size. The average radius determined for the synthesized NCs with the image is $\sim 1.04 \pm 0.14$ nm with a polydispersity of $\sim 13\%$



Figure 2.5 TEM for a) synthesized CdSe NC b) small commercial CdSe NCs.

2.8 X-ray photoelectron spectroscopy (XPS)

XPS sample preparation were done by suspending all quantum dots samples in Toluene. P-doped silicon oxide wafers were cleaned with an AMI (Acetone, Methanol, Isopropanol) washing protocol and were dried under nitrogen. 150 mL of the quantum dot suspension was drop-cast onto a wafer, and the wafer was dried under vacuum for 48 hours prior to XPS measurements.

XPS spectra were acquired using a Thermo Scientific K-Alpha spectrometer (Al Ka). The X-ray spot size was 400 μ m², and a low-energy electron flood gun was employed for charge neutralization. High resolution scans of the Cd and Se regions were taken using a 0.1 eV bandpass and analyzer pass energy of 50 eV.

Figure 2.6 shows the XPS data for commercial and synthesized small CdSe NCs. The Cd 3d 5/2 peak were observed in the range 404 eV – 406 eV centered with normal distribution at 405.0 ± 0.2 eV and the Se 3d peak 53 eV – 56 eV centered with normal distribution at 54.6 ± 0.2 eV which agree with previously reported values³⁷⁻³⁸.



Figure 2.6 XPS spectra comparison for synthesized CdSe NCs (2.5a and 2.5c) and commercial CdSe NCs (2.5b and 2.5d) showing Cd 3d5/2, Cd 3d 3/2 and Se 3d peaks.

2.9 Resonance Raman Spectroscopy

For resonance Raman measurements, the samples were first treated with a ligand exchange procedure to quench the extensive background fluorescence using thiophenol as quenching ligand. An aliquot of synthesized CdSe NCs was mixed with thiophenol as a quenching ligand at room temperature. The mixture was then mixed with MeOH, centrifuged at 10,000 rpm and resuspended in a small amount of Toluene. The samples were then prepared by depositing 50µL of the ligand exchanged NC on a clean p-doped Si wafer and dried under ambient conditions. The Raman data was obtained using a Horiba LabRam HR800 microscope using a 473nm Ciel Laser.

The Longitudinal-optical mode of bulk CdSe is observed at ~ 209 cm-1. The Raman spectra of small CdSe NCs compared to commercially available CdSe NCs with sub-nm radius is shown in Figure 2.7. The fundamental of the LO phonon mode is clearly observed in both samples at ~ 206 cm-1 along with the first overtone at ~ 409 cm-1. The Raman phonon modes of small CdSe NCs is known to be redshifted in energy compared to larger NCs as well as their bulk form due to the negative phonon dispersion.



Figure 2.7 Resonance Raman spectrum showing the characteristic LO phonon modes in commercially available CdSe NCs compared to synthesized CdSe NCs of similar size.

2.10 Conclusion

In conclusion, this chapter shows a reproducible synthesis for small NCs in the molecular cluster regime. These NCs have a good size distribution as well as show all characteristic features which determine the quality of the samples. The XPS and Raman characterization data confirms that the such samples can be synthesized with superior quality. Further this chapter describes the various method and techniques used to characterize and study the NCs.

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CHAPTER 3

Extending Semiconductor Nanocrystals from The Quantum Dot Regime to The Molecular Cluster Regime.

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The size-dependent optical and electronic properties of semiconductor nanocrystal (NC) have been exploited over decades for various applications. This size dependence involves a transition from the regime of bulk colloids of ~100 nm radius to quantum dots (QDs) of ~10 nm radius, the details of which are material specific. This chapter discusses the transition from the QD regime (~10 nm) to the molecular cluster regime (~1 nm) of nanocrystals. Carefully synthesized set of CdSe nanocrystals with sizes ranging from 0.89 to 1.66 nm in radius are discussed. As the nanocrystals become small, the surface emission

strongly increases in amplitude, and the core emission broadens and red-shifts. These effects are rationalized in terms of coupling to ligands via electron transfer theory described in chapter one. The core emission spectra arise from increased vibrational coupling of ligands for very small NC. The surface emission amplitudes arise from a size-dependent surface free energy. The transition from the QD to the molecular cluster regime is found to be at 1.2 nm radius, in contrast to the transition from the bulk to QD transition at the Bohr radius of ~5.4 nm in CdSe. These size-dependent surface electronic phenomena may be used for potential light emission applications.

3.1 Introduction

Colloidal semiconductor nanocrystals (NCs) have potential applications in light generating technologies such as solid state lighting, high performance LEDs ¹⁻⁵ and lasers⁶. The spectral tuneability and narrow emissive linewidths allows for a large colour gamut for display device applications. Near unity quantum yields and precise control of the excitonics are made possible through synthetic advances⁷. Moreover, colloidal NCs are inexpensive in comparison with NCs grown with other techniques such as molecular beam epitaxy (MBE), and can be altered though surface ligand modification.⁸⁻¹²

The size dependent properties of semiconductor NCs have been extensively studied for over two decades.¹³⁻¹⁵ The size dependence in NCs dictates their

absorption and photoluminescence (PL) spectra from excitons confined to the core. The regime of nanocrystals largely explored involves the transition from the bulk, to the quantum dot (QD) regime. A similar understanding of the transition from the QD regime to the molecular cluster regime is essential for better understanding the properties of smaller NCs.

Based upon the understanding and control of nanocrystals at the QD regime, current applications employ the spectrally narrow emission from the core exciton of these semiconductor NCs^{1, 16-19}. As discussed in above chapters, these NCs are also known to emit light from their surface that is broadened and redshifted with respect to the well-known emission from the excitonic core. Our group has shown that this surface PL arises from surface states of the NC that are electronically coupled to the core excitonic states²⁰⁻²³.

In contrast to the applications based on understanding and controlling the core emission of NCs, this portion of the thesis presents an opportunity to rationally exploit aspects of surface emission based upon understanding their electronic properties. The size dependent control of surface emission can provide small NCs as potential candidate in light emission for display, lighting, sensing and variety of other applications with a focus on the surface of such NCs. The surface emission of CdSe NCs have recently been exploited to develop white light sources for displays, lighting, and even optical thermometry.^{5, 21, 24-25} Size dependent control of white light emission from CdSe NCs can further be engineered using temperature as well as ligand surface chemistry²¹ as show in chapter one.

This chapter explores the size dependence of CdSe semiconductor nanocrystals from the quantum dot regime (~ 10 nm) to the molecular cluster regime (~1 nm) and reveal that this size dependence may be rationalized in terms of theory as well as exploited for lighting and display applications. It is shown that with careful growth and experiments, this transition from QD to molecular cluster regime can be better understood. In this regime, the smaller sized NCs with large surface area show an increase in light emission. This strong size dependence is rationalized to difference in Gibbs free energy (Δ G) between core and surface states, which could lead to applications in superior white light generation with single NCs.

3.2 Results and Discussion

The size of these ultra-small NCs can tune the dual emission to change the degree of white light produced over CIE coordinates (Commission internationale de l'éclairage) which is generated using a single emitter. Figure 3.1 presents the size dependence of the photoluminescence spectra and its CIE representation to show the strong size dependence of a set of tetradecylphosphonic acid (TDPA) capped CdSe NCs. Figure 3.1a schematically illustrates the transition of small NCs bound with ligands to a more molecule like size regime. Figure 3.1b, shows

the normalized PL and absorption intensities for NC size ranging from (0.89 nm to 1.66nm). The size of the NCs was determined using the empirical equations proposed by Yu *et al.*²⁶



Figure 3.1 The transition to the molecular limit is illustrated by photoluminescence (PL) spectra. a) Illustration showing evolution to molecular cluster regime in small NCs bound to ligands. b) Size dependent PL and absorption spectra showing more surface PL, the blue region shows the onset of evolution of surface emission. c) CIE 1931 plot showing different regions A (QD regime) and B (molecular cluster regime) with size dependent light generation from NCs. The size of the points is relative to the size of the nanocrystals. CIE coordinate trajectory shows the evolution from the QD regime to the molecular cluster regime. Reprinted with permission from Jethi et al., "Extending Semiconductor Nanocrystals from The Quantum Dot Regime to The Molecular Cluster Regime", The Journal of Physical Chemistry C, 2017 Copyright © 2017 American Chemical Society Smaller sized NC display two emission bands, a narrow core emission and a secondary broad and redshifted emission from surface state. As the size of the NC decreases, increased surface emission as well as a blue-shift in core emission wavelength is clearly observed.

A corresponding blue-shift is present in the absorption spectra. The surface of the NCs is dominant in defining many chemical and physical properties which play a key role in tuning and designing functional NCs.²⁷⁻²⁸ Although there is no observable surface emission for larger sized NCs at room temperature, it is present at lower temperatures²³. The onset of surface emission at room temperature can be observed below 1.2 nm. It further evolves as the radius is reduced to sub-nanometer range.

Figure 3.1c, shows the CIE chromaticity of the PL spectra for different sized NCs. The degree of whiteness of the emission can be controlled by monitoring the size of the NC in the ultra-small regime. Larger NCs show narrower emission in green and red regions of CIE. It has been previously shown that the color generation of ultra-small NCs can be further controlled by changing the surface chemistry and the type of binding of surface ligands.²⁹⁻³¹ Such control can be valuable in generating white light without the need of phosphors or multiplexing. The data reveals different regimes. The larger NCs at the edge of CIE produce saturated colours (Region A) which correspond to the QD regime. In contrast, the smaller

NCs shown in Region B, generate varying degrees of white color. The CIE coordinate trajectory monitors the evolution from the QD regime to the molecular cluster regime. Both regions A and B are controllable over the CIE with size and composition of NCs.

To explore this evolution from QD to molecular cluster regime, the full width at half maximum (FWHM) of emission spectra and Stokes shift were respectively plotted as a function of radius. Figure 3.2a shows the size dependence on the FWHM of the core emission (Γ_{core}). The values Γ_{core} for larger NC are consistent within the QD regime. As the radius is decreased, an increase in Γ_{core} value from 100 meV to 200 meV is observed. CdSe NCs are known to exhibit a Stokes shift (δ_{core}) which is a combination of radiative decay from lower energy level interactions with phonons and/or radiative decay from dark to bright exciton states³²⁻³⁴. The magnitude of δ_{core} (~10-40 meV) for larger NCs (>1.2nm radius) is consistent with previously reported values. These studies show that Stokes shifts are higher for small NCs.³⁵⁻³⁹ As the radius approaches ~ 1.2nm, an increase (~140 meV) in δ_{core} is observed (Figure 3.2b). Both Figure 3.2a and 3.2b show a clear change for radii < 1.2nm.

The origin of the linewidth and Stokes shift of NC in the QD regime has been well discussed.³⁴ These observables arise from inhomogeneous broadening and homogeneous broadening mechanisms. Figure 3.2c shows the relation between δ_{core} and Γ_{core} . It is observed that δ_{core} shows a linear trend with Γ_{core} above 150

meV. The Stokes shift can be expressed in terms of the Huang-Rhys parameter (S), which is a metric for the electron-phonon coupling. The relation between the Stokes shift and Huang-Rhys parameter is given as δ =(2S-1) $\hbar\omega$ or δ =2S $\hbar\omega$ ⁴⁰⁻⁴¹.



Figure 3.2 Broadening and red-shifting of PL spectra reflects coupling of core to ligands. a) FWHM of the core as a function of size. The change in FWHM trend is illustrated with the shaded region near 1.2 nm. b) Core Stokes Shift as a function of size of NCs c) Stokes shift vs FWHM of the core state showing a linear trend in the molecule-like regime(blue). d) CdSe semiconductor NCs sizing curve showing different size regimes in NCs. Reprinted with permission from Jethi et al., "Extending Semiconductor Nanocrystals from The Quantum Dot Regime to The Molecular Cluster Regime", The Journal of Physical Chemistry C, 2017 Copyright © 2017 American Chemical Society

To further analyse this evolution, a standard sizing curve was plotted using the empirical fitting function detailed by Yu *et al.*²⁶ which relates the size and the wavelength of the first excitonic peak of the CdSe NCs (Figure 3.2d). Noted are the different regimes corresponding to confinement in NC. The dotted red line marks the Bohr radius of bulk CdSe at ~ 5.4 nm above which weak confinement is observed. As the size of the NC is reduced into the strong confinement regime, a blue shift in the first excitonic absorption peak is observed. Further reduction in size (sub 1.5 nm, dotted blue line) shows a strong size dependence where the absorption peak shifts dramatically to higher energies.

To rationalise the size dependence in terms of the energy difference (Δ G) between the core and the surface states, consider the temperature dependence small NCs using semi-classical electron transfer scheme based on the work of Marcus and Jortner^{21, 23, 42}. Recall chapter one, equation 1.11 and figure 1.10

$$\frac{1}{\tau_{ET(forward)}} = \frac{1}{\tau_f} \left(\frac{\pi}{\hbar^2 \lambda_m k_b T}\right)^{\frac{1}{2}} e^{-S} \times \sum_n \frac{S^n}{n!} e^{\frac{-(\Delta G + \lambda_m + n\hbar\omega)^2}{4\lambda_m k_b T}}$$
(1.11)

where ΔG represents the energy difference between the 1S and the surface state, λ_m represents the medium reorganization energy and the Huang-Rhys coupling parameter, S represents the internal quantum mode.



Figure 3.3 Surface to total integrated areas of emission band (A_S/A_T) as a function of Temperature at varying Gibbs surface free energy (ΔG). Details of the calculation are shown in Appendix A, supporting information for chapter 3. Reprinted with permission from Jethi et al., "Extending Semiconductor Nanocrystals from The Quantum Dot Regime to The Molecular Cluster Regime", The Journal of Physical Chemistry C, 2017 Copyright © 2017 American Chemical Society

 ΔG is a significant parameter which influences the temperature dependent ratios of PL emissions. Figure 3.3 calculates the surface to total ratio (A_S/A_T) of integrated areas of the PL emission using Marcus-Jortner electron transfer theory assuming a steady-state three state model; Ground state (GS), excited core state (1S) and exited surface state. It is observed that the A_S/A_T increases as a function of ΔG for all temperatures. The data presented above reveals a strong size dependence to the surface spectra. It is observed that the surface emission spectra, unlike the core emission, does not broaden or redshifts for different sized NCs. In contrast, the surface emission amplitude increases as the size of the NC is reduced. One might naively anticipate that the rise in amplitude is due to increased number of surface sites, which should effectively change the spectral features as well. As no broadening or shifts are observed in the surface emission spectra, it can be concluded that the reorganization energies are not changed based upon NC size. As shown by theory, the broadening and red shifting of the surface band largely arises from the reorganization energies from the classical bath and the quantum vibrations. Since the reorganization energies are independent of particle size, the remaining parameter in the theory is the free energy difference.

The rise in the amplitude can be modeled via changes in free energy (Δ G) between the core and the surface states. To analyse the amplitude of the surface emission spectra, the integrated areas of the surface band relative to the total emission (A_S/A_T) as a function of radius are explored (Figure 3.4a). A strong and monotonic decrease in the A_S/A_T with radius is observed. To ensure that the size dependence of the surface band amplitude is not contaminated by differences in temperature dependence, Figure 3.4b shows a subset of the NC PL ratios as a function of temperature. These results are consistent with our prior works which focused on the thermodynamics in more detail ^{5, 23, 30}



Figure 3.4 Thermodynamics rationalizes the surface PL, and the transition point. The transition radius is ~ 1.2 nm for 300K. a) Integrated areas of the surface band relative to the total PL emission, A_S/A_T as a function of radius, R. b)
Temperature dependence of A_S/A_T for different sized NCs c), Calculation showing A_S/A_T as a function of ΔG d) ΔG values extracted from A_S/A_T for different sized NCs. Reprinted with permission from Jethi et al., "Extending Semiconductor Nanocrystals from The Quantum Dot Regime to The Molecular Cluster Regime", The Journal of Physical Chemistry C, 2017 Copyright © 2017 American Chemical Society

The semi-classical electron transfer theory as described in chapter one^{21, 23, 42} describes the surface PL spectra and amplitude. To assess the influence of ΔG
on size dependent properties of these ultra-small NCs, values for A_S/A_T with varying ΔG using semi-classical electron transfer theory were computed (Figure 3.4c). Assuming the PL ratio is governed by ΔG , the experimentally observed PL ratios can then be used to extract an experimentally determined ΔG . These ΔG values when extracted from the experimental A_S/A_T for different sized NCs, show a strong dependence to the radius (Figure 3.4d). This analysis suggests that the strong size dependence of the PL ratios arises from a size dependence to the free energy of the surface electronic state.

3.3 Conclusion

The evolution of semiconductor nanocrystals from the bulk to the quantum dot regime is well understood. In contrast, our understanding of the transition from the quantum dot to the molecular cluster regime is in its early stages. These data on CdSe NC reveal the surface effects on the core and the surface emission bands. It is observed that the emission linewidths and Stokes shift are dictated by the surface of NC. The core emission band reveals increased coupling to ligands at the surface of the NC. The surface emission band reveals that the surface electronic state has a size dependent free energy. Through careful experimental growth techniques, a series of ultra-small NCs can be synthesized with strong size dependent properties. These NCs are dominated by various surface effects that come in to play in this regime. Ligand interactions are more enhanced as these NCs are composed of limited number of atoms which make up most of the surface.⁴³⁻⁴⁴ Detailed computational and modelling can probe the significance of surface free energy in tuning such NC systems. This work suggests a path towards rational use of surface and molecular effects for light emissive applications.

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CHAPTER 4

The effect of Exciton-Delocalizing Thiols on Intrinsic Dual Emitting Semiconductor Nanocrystals

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As described in chapter one, the surface ligands play a vital role in directly influencing the optical properties of NCs. The so-called trap states that lie between the HOMO and LUMO of the quantum confined orbitals of the NCs can trap electrons or holes and change the PL of NCs. Alkanethiol ligands are known as hole – trapping ligands as they quench the luminescence of CdSe NCs. This chapter discusses the effect of thiol ligands on the small NCs. The results show that such ligands can influence the quantum yield, thermodynamics of core and surface PL as well as delocalize the exitonic wavefunction.

4.1 Introduction

Passivating ligands on semiconductor NC play an important role in tailoring optical processes in NCs¹⁻². The influence of ligands on exciton relaxation dynamics, surface trapping, and delocalization remains an important area of research.³⁻⁸ Thiols ⁹⁻¹⁰ have traditionally been viewed as a poor ligand choice for CdSe NC systems, primarily due to low reported PL quantum yields. Wuister et al.¹¹ argued that the PL quenching was due to the energetic position of the thiol HOMO, which was assumed to lie above the valence band-edge of CdSe NCs, causing the ligand to behave as hole trap. Hole trapping can occur on a thiol ligand if a thiol redox energy level is higher than the valance band of the semiconductor¹¹. In CdSe NCs this process is energetically favored and can possibly lead to conversion of thiols to disulfides through a photocatalytic reaction ¹²⁻¹³. The case of CdSe systems were compared with thiol-capped CdTe systems which displayed increased luminescence, and whose valence band is known to be positioned at higher energies. While such a picture remains an effective first-approximation, it has been shown that the HOMO levels of several thiols are actually within the valence band of CdSe NCs, and thus there is a need for a more nuanced understanding of the thiol interaction.¹⁴ In particular, the work in this chapter was motivated by a work which has modelled the interaction of the bound thiol in terms of orbital mixing between the HOMO of the thiol and the density of states of the CdSe valence band ^{10, 14-16}. Through ligand-exchange, the excitonic hole confinement can be altered based on the HOMO of the thiol

ligand, as well as the extent of thiol ligand exchange. It is within this context that this chapter addresses the temperature dependent emissive properties of thiol-capped dual emitting CdSe NCs ¹⁷⁻²¹ that exhibit narrow core state emission and broad redshifted surface state emission. Such an approach will probe the interplay between the core and surface state, as delocalization of the excitonic hole should perturb the recombination rates of the core and surface states independently.

4.2 Results and Discussion

In order to study the effect of thiols, three distinct thiols based on relative differences in their steric bulk and electronic properties: 1-Dodecanethiol (DDT), 1-Adamantanethiol (ADMT) and Thiophenol (PhS) were selected. Surprisingly, the data reveal that even at partial ligand substitution, ADMT can be used to increase the overall PL QY of these dual emitting CdSe NCs while delocalizing the excitonic hole, leading to a spectroscopic red-shift of both core and surface emission. Such an observation is found to be consistent with the work of Rosson et al.,¹⁹ who observed a similar PL enhancement employing a mixture of DDT and formic acid. These results reinforce the picture of a radiative surface state, in which the electron is tied to a cadmium trap state.²²

The room temperature optical properties of thiol-exchanged dual emitting CdSe NCs in toluene are shown in Figure 4.1. Figure 4.1a shows normalized absorbance spectra. In contrast to the original TOP (here denoting phosphonates

and/or phosphine passivation) sample, the ADMT and DDT samples exhibited a redshifted absorption peak. The origin of this redshift has been explained by Frederick et al¹⁴, and is related to the orbital mixing between the thiol HOMO and the CdSe valence band. In order to study the effect of the thiols on the photoluminescence properties of dual emitting NCs, steady state fluorescence measurements were performed (Figure 4.1b) and the relative quantum yields were determined (Figure 4.1c) with quinine sulphate reference standard.

In the case of the DDT passivated NCs, the core emission intensity decreased significantly, while the surface emission intensity was only slightly lowered. A similar response was also seen with PhS with no observable core emission (see Appendix A, Supplementary Information for chapter 4). Fluorescence lifetime measurements of the core state were performed to ensure that the PL changes were due to an increase in the non-radiative rate. The time correlated single photon counting (TCSPC) data show the time resolved decay of the core state in all the three samples (Figure 4.1d). In the case of DDT, there is a significant decrease in the measured core state lifetime, whereas the ADMT capped NCs lifetime was slightly higher than the original sample. The lifetimes were calculated through a weighted average of the decay rates obtained from a tail-fitted bi-exponential fit.



Figure 4.1 Room temperature data before (TOP) and after ligand exchange (DDT/ADMT) a) Normalized absorption, b) Normalized PL, c) Surface and Core QY relative to total QY d) TCSPC data showing PL decay curves. Reprinted with permission from Jethi et al., "The effect of Exciton-Delocalizing Thiols on Intrinsic Dual Emitting Semiconductor Nanocrystals", ChemPhysChem 2016, 17, 665. Copyright © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

The fluorescence data taken from the NCs suspended in toluene are tabulated in Table 4.1. The DDT NCs exhibited the smallest Stokes shift, whereas the original TOP capped dots exhibited the highest shift. The size dependent origin of the non-resonant Stokes shift for phosphonates capped CdSe NCs has previously been investigated Efros et al.²³⁻²⁴ The authors reported that CdSe NCs with radii of approximately 1 nm possessed a non-resonant Stokes shift of approximately 100 meV. Given that the addition of a thiol ligand serves to delocalize the hole, creating a greater effective radius, we suspected that the change in Stokes shift can be partially attributed to the size dependent splitting of the ± 2 states. However, it appears that this data cannot be described by size dependence alone.

Table 4. 1 Room temperature fluorescence data for dual emitting CdSe NCspassivated with TOP/ADMT/DDT

Thiol	Core Lifetimes (ns)	Stokes Shift (meV)	∆(Core-Surface) (meV)	Surface FWHM (meV)	Core FWHM (meV)
TOP	126.4	240	450	620	230
ADMT	131.4	150	570	580	230
DDT	44.2	110	630	590	310

The data shows a Stokes shift difference of 130 meV between the TOP and DDT passivated sample. It is suspected that specific ligand-surface interactions may also play a role in determining the Stokes shift. This hypothesis is seemingly supported by the trend in the difference between the core and surface emission

energies ($\Delta_{\text{Core-Surface}}$), which was found to be the opposite of the Stokes shift trend. It is speculated that this is caused by differences in the ligand stabilization of the Cd surface trap state. The increased polarity of the phosphonate groups attached to the cadmium should raise the energy of a Cd acceptor state.¹⁹ This trap state may be lowered in energy if the phosphonate is replaced by a thiol group, perhaps further stabilized through π-bonding character of the thiol.¹⁶ These results of the non-resonant stokes shift propose that the ligands have a significant contribution to the observed shifts, which may also include solvatochromic effects.²⁵

As shown in chapter one, the temperature dependent emission of small NCs may be inherently tied to chemical nature of the ligand species present¹⁸. In order to further explore the ligand's influence on such a system, low temperature PL measurements were performed. Such measurements can be used to investigate the specific surface-ligand interactions. Thiol passivated NCs exhibit particularly strong coupling that can be seen from spectroscopic shifts. Figure 4.2 a, b and c show the temperature dependence of the PL for the three samples embedded in a polystyrene matrix.



Figure 4.2 Temperature dependent PL a) TOP b) ADMT and c) DDT. Reprinted with permission from Jethi et al., "The effect of Exciton-Delocalizing Thiols on Intrinsic Dual Emitting Semiconductor Nanocrystals", ChemPhysChem 2016, 17, 665. Copyright © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Figure 4.3a shows the surface-to-core ratios of the integrated areas of the PL as a function of temperature. It was observed that the ratio increased monotonically as the temperature dropped to 80K. This have been previously explained in terms of a thermodynamic equilibrium of carriers in the core and the surface states ^{17, 26-27}. Lower temperature thus favours the occupancy of the surface state, which is lower in energy than the core state.²⁸ The data showed that NCs passivated with thiols displayed higher temperature dependant surface to core ratios in comparison with the native TOP sample. This can be attributed to a larger energetic separation between core and surface states ($\Delta_{Core-Surface}$) as previously discussed.

As per the model discussed in chapter one²⁶, the free energy difference between core and surface state (Δ G) is a key parameter that influences the temperature dependant ratios of integrated surface and core emission. It is assumed that the Δ _{Core-Surface} shift is proportional to a change in Δ G between the core and the surface states. To qualitatively assess the impact of Δ G on the surface to core ratios, model calculations were performed. (Fig 4.3b). The results of this simulation can account for the observed trend of surface to core ratios for TOP, ADMT and DDT, which is one of the parameters influenced by the Δ G values (lowest for TOP and highest for DDT).



Figure 4.3 a) Temperature dependent ratio of Integrated areas of Surface and Core emission b) simulation of change in surface to core ratio with different ∆G values. Reprinted with permission from Jethi et al., "The effect of Exciton-Delocalizing Thiols on Intrinsic Dual Emitting Semiconductor Nanocrystals", ChemPhysChem 2016, 17, 665. Copyright © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

To further analyse the overall emissive increases of the surface PL, Figure 4.4a, shows the relative increase of the surface PL as a function of temperature. The relative increase in surface emission was greatest for the DDT sample, which had the lowest PLQY at room temperature, and lowest for the ADMT sample which had the highest PLQY at room temperature. This seems to suggest that the impact of non-radiative recombination was greatest for DDT, which agrees with the reduced PLQY at room temperature. It is also noted that the thiol capped NCs displayed temperature dependant spectral shifts that differed from the native TOP sample (Figure 4.4 b, c and d).



Figure 4.4 a) Relative integrated surface intensities with respect to room temperature before (TOP) and after ligand exchange(DDT/ADMT), Temperature dependent PL normalized to surface emission b) TOP, c) ADMT, d) DDT showing the blue-shift in the surface state as the temperature is reduced to 80K.
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The origin of temperature dependent blue-shifted emission in bulk semiconductor systems is related to a thermal contraction of the lattice, which leads to an increased semiconductor bandgap.²⁹⁻³⁰ This effect also appears in quantum confined semiconductor crystals.¹⁷⁻¹⁸ The change in core and surface emission blue-shifts per kelvin (dE/dT) are summarized in Table 4.2 for TOP, ADMT and DDT (only dE/dT surface emission blue shift is shown for DDT as the core emission is almost quenched at lower temperatures). The increased blueshift of the thiol samples can be explained in terms of a lower orbital mixing of the thiol HOMO with the valence band density of states. At room temperature, the strong mixing creates a hybridized orbital which delocalizes the hole into a higher energy.¹⁴ When the temperature is lowered, the density of states of the NC is altered. This can decrease the extent of orbital mixing, hence reducing the hole delocalization. This process is depicted in Figure 4.5



Figure 4. 5 Schematic representation of alignment of energy bands at 293K and 80K. The dark regions in the valence band correspond to the higher density of Se 4p states which can mix with the thiol HOMO to split into hybridized orbitals. At 80K the bandgap increases, the valence band will shift to lower energies as a result, and the thiol HOMO will no longer be optimally aligned. Reprinted with permission from Jethi et al., "The effect of Exciton-Delocalizing Thiols on Intrinsic Dual Emitting Semiconductor Nanocrystals", ChemPhysChem 2016, 17, 665. Copyright © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 4.2 dE/dT	values for sur	face and cor	e emission	blue-shift for	[.] dual	emitting
	CdSe NCs pa	assivated wit	h TOP/AD	MT/DDT		

Thiol	dE/dTCore (meV/K)	dE/dTSurface (meV/K)			
ТОР	0.43	0.24			
ADMT	0.49	0.63			
DDT	-	0.62			

The surface blue-shift was ~53 meV for TOP, whereas it was nearly three times higher for the thiol samples, ~140 meV for ADMT and DDT. This indicates that the surface PL shift cannot be described well based on the valence band shift alone, as it was in the case of the core emission. The data suggest that the energy of the surface state for thiol capped NCs is raised in energy. This proposes a strong temperature dependence of the bonding interaction between a thiolate and the Cd surface atoms. Furthermore, the independent blue-shifts for both the core and surface states suggest that the surface is not related to pinned defect state emission.²⁶ Such an observation may suggest the existence of surface excitons.³¹ This result should be amenable to further computational studies.³²⁻³⁶

While the semi-classical electron transfer model rationalizes the observations here, an in depth understanding of specific chemical details is lacking. Further, the chemistry that may associate to the physical model for the observed spectra is explored. Frederick et al. noted that the extent of red-shift in the absorbance data for dithiocarbamate capped NCs was related to the level of the HOMO.¹⁶ The greatest shifts were associated with lower energy HOMO levels (i.e. more negative). In order to verify if the absorbance red-shifts observed in the data were consistent with this observed trend, density functional theory (DFT) calculations to calculate the HOMO levels of the unbound protonated thiols used in this study were performed. These results were compared to values in the literature³⁷, and are presented in Appendix A, supplementary information for chapter 4. In both cases, the observed order of the levels was identical. It was noted that although this is not an accurate estimate of the energies of the surface bound thiols (or thiolates), it is suspected that the order will be conserved. It was found that the calculated HOMO of PhS was the highest of the thiols studied, whereas DDT has the lowest HOMO.

In the case of PhS, the sulphur atom is resonance stabilized by the electron donating benzene ring¹¹, thus raising the energy of the HOMO in contrast with the other thiols studied. The increased electron density on the sulphur atom make it a potent hole trap, and this also explains why the PhS sample displayed no core emission. In the case of the DDT passivated NCs, the core emission decreased significantly, while the surface emission was slightly lowered. Conversely, the ADMT passivated sample showed an enhanced PL response, where the core emission increased slightly in comparison to NCs with TOP. This was accompanied by an increased surface state emission. The fact that the core of DDT is quenched more rapidly than the surface emission may be tied to the poor overlap between the core wave-function and the newly delocalized hole.³⁸ Based on the results from DDT and ADMT, it can be concluded that the surface exciton is not affected to the same extent by the hole delocalization as the core exciton. These results showed that in the case of DDT, the decrease in PL QY was tied to non-radiative decay of the core exciton.

To monitor the ligand substitution, XPS measurements were done. (See Appendix A, supplementary information for chapter 4). In the case of ADMT, the fraction of ligand exchanged appears to be low. This can be deduced from the high amount of remaining phosphorus signal, indicating that a high amount of TOP and phosphonates remained. DDT, on the other hand, had a much lower phosphorus signal indicating that a majority of the phosphonates were substituted.³⁹ It is suspected that the reason for the low substitution of ADMT compared to DDT is related to steric bulk. The work of Owen shows that surface Cd²⁺ atoms must be passivated by two X-type anionic in order to conserve charge neutrality.⁴⁰ If ADMT is binding as a thiolate, it will be sterically unfavorable to bind two ADMT ligands to the same Cd²⁺ surface atom. Despite the presumed low degree of substitution, the influence of the ADMT on the excitonic properties remains pronounced. This is explained by Amin et al.4¹⁰, who proposed that the hole delocalization is associated with thiolate binding, and that the macroscopic hole delocalization is a function of the fractional surface occupation of these ligands. It is surmised that this may be as equally important as the

HOMO level in contributing to the observed red-shift. Moreover, while heterogeneous surface coverage via mixtures of ligands may appear undesirable, it is stressed that passivating the surface with multiple types of ligands may lead to complimentary and/or synergistic effects. Such a strategy has been used to produce CdSe NCs with near unity quantum yields.⁴¹

4.3 Conclusion

In conclusion, this chapter shows that ligands have a profound influence on the excitonic properties of the nanocrystal. The earlier work from Weiss that ligands can delocalize the excitonic wave function is confirmed. Further, ligands can strongly affect the total and relative quantum yields, the thermodynamics of core and surface equilibria, and influence the blue-shifting of the surface PL with temperature in a manner consistent with delocalized or excitonic states. Through unconventional thiol ligands it will be possible to probe the exciton dynamics CdSe NCs with intrinsic dual emission. Heterogeneous ligand passivation consisting of thiolates and phosphonates show promise as they redshift the emission and can be used to tune the relative amounts of core and surface emission. Computational studies should provide insight into this phenomenon.

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CHAPTER 5

Towards Ratiometric Nanothermometry via Intrinsic Dual Emission from Semiconductor Nanocrystals

This chapter was partially adapted with permission from Jethi et al., "Towards Ratiometric Nanothermometry via Intrinsic Dual Emission from Semiconductor Nanocrystals", J. Phys. Chem. Lett., 2015, 6 (4), pp 718–721. Copyright © 2015 American Chemical Society

The previous chapters talk about the effect of size and ligands on the surface of small semiconductor NCs. The coupled nature of core and surface emission based on temperature dependence of PL spectra using the theoretical model is also described in chapter one. This part of the thesis discusses the application of small semiconductor NCs in optical nanothermometry. The chapter one shows that the small NCs exhibit intrinsic dual emission from the exitonic core as well as the surface. The dependence of coupled surface and core PL on temperature is exploited to be used a temperature sensor. The sensitivity and reproducibility of the NC system is discussed along with aging and reusability. The results reveal

that such a sensor can be used over broad temperature range and is fairly robust.

3.1 Introduction

Optical thermometry is one of the areas of research which has been extensively investigated for measurements of temperature in unusual environments, spanning living cells to aircraft wings¹⁻². Interpretation of thermodynamically controlled emission spectrum can lead to precise measurement of temperature profiles. Since the emitters are spatially localized, one can either measure spatially distributed temperature profiles, such as in structural applications or, one can measure temperature of highly localized environments, specifically applicable to biological and medical imaging.

Semiconductor NCs have been used as optical thermometers in various guises for their features that are attractive for such applications. The use of NC in optical thermometry has been discussed in detail in the literature¹⁻⁷. In the earliest implementations, the temperature dependence of the photoluminescence (PL) intensity or wavelength was monitored. In NC with low PL quantum yield at room temperature (5%), the PL can increase to near unity at cryogenic temperatures. Alternatively, the PL wavelength blue shifts at lower temperatures. Either parameter has been used towards NC based thermometry.

142

An ideal optical thermometer utilizes ratiometric measurements, a system in which an output is directly proportional to an input. Changes in the sensor local environment causing inaccurate temperature can often be overcome using ratiometric detection schemes. Hence, these single parameter measures of NC emission need to be extended to enable some form of ratiometry. Intrinsic dual emission from two thermodynamically coupled sub-states within the NC enable such ratiometric measurements to be performed, thereby improving measurement sensitivity and robustness to fluctuations. One such example was shown by McLaurin et al. using Mn-doped ZnS based NC⁵⁻⁶. With careful engineering of doping and layering, PL was observed from both the dopant as well as the excitonic core of the NC. These two bands arise from states that are in thermal equilibrium as indicated by the temperature dependence of the relative intensity of the two PL bands. Other variations on this theme have recently been implemented^{3, 7}.

This chapter describes a completely new way to monitor temperature ratiometrically via intrinsic dual emission from semiconductor NCs. As described in the introduction, semiconductor nanocrystals are known to emit light from their surface that is broadened and redshifted with respect to the well-known emission from the excitonic core. Pertinent kinetics and energetics allow these two PL bands arise from states that are in thermodynamic equilibrium. Therefore, the dual emission from the NC can be exploited as a ratiometric temperature sensor. Since dual emission character is derived from the surface, nominally considered defect states, it is not clear that this approach can be practically implemented in a sensing application. Variations and degradation of the surface via processing and aging may render the character of this dual emission to be uncontrollable. This chapter describes that CdSe NC with intrinsic dual emission from the core and surface form stable and reproducible temperature sensors.

3.2 Results and Discussion

Figure 5.1 shows how ratiometric optical thermometry may be implemented in a general scenario. Figure 5.1a shows a diagram that illustrates the electronic states and the transitions between them. The two emissive states that are in thermal equilibrium which are separated by some thermally accessible energy, ΔE_{kT} . The difference in the emission wavelengths, ΔE_{opt} is equal to ΔE_{kT} . Figure 5.1b shows a schematic representation of emission from two states that are energetically separated by ΔE_{kT} , with some linewidth δE . The emitted spectrum will be a Boltzmann weighted sum of the contributions from the two bands. This approach enables ratiometry to extract temperature. However, the contrast ratio will be dictated by δE relative to ΔE_{opt} , as shown in the inset. Although, this general approach is theoretically valid, it will not enable viable implementations of optical thermometry with good contrast, range, and sensitivity.


Figure 5.1 (a) A general energy level scheme describing dual emission from one system. A thermal energy difference (ΔE_{kT}) is equal to the optical energy difference (ΔE_{opt}) between two emitting levels that are in thermodynamic equilibrium. (b) A schematic illustration of the two emissive bands, noting ΔE_{opt} as well as the linewidth (δE). Inset shows the contrast is dictated by δE relative to ΔE_{opt} . (c) A semiclassical electron transfer scheme for describing dual emission from the excitonic core as well as the surface of a semiconductor nanocrystal. (d) A schematic illustration of emission of the two bands. In this case, $\Delta E_{opt} >> \Delta E_{kT}$. Reprinted with permission from Jethi et al., "Towards Ratiometric Nanothermometry via Intrinsic Dual Emission from Semiconductor Nanocrystals", J. Phys. Chem. Lett., 2015, 6 (4), pp 718–721. Copyright © 2015 American Chemical Society An alternative approach is shown in Figure 5.1c. which illustrates a semiclassical electron transfer (ET) scheme that follows the work of Marcus and Jortner⁸⁻⁹ as shown in chapter one. This model can describe the temperature dependence of the dual emission that appears to be intrinsic to semiconductor NC^{8, 10-12}. The key aspect to this configuration coordinate approach is that now ΔE_{opt} is no longer equal to ΔE_{kT} . The two emissive states in NC correspond to the band edge exciton from the core, and the surface state. These two states are energetically separated by ΔE_{kT} . This energy difference gives rise to the relative intensities of the two bands – thereby enabling ratiometry as above. Due to vibronic coupling, the final states are also distinct here. Hence, $\Delta E_{opt} \gg \Delta E_{kT}$. Figure 5.1d shows a schematic representation of this situation. With vibronic coupling, a large ΔE_{opt} is obtained thereby enabling better contrast as shown in the inset.

Figure 5.2a shows PL spectra of CdSe NC synthesized as described in chapter 2 at a variety of temperatures. The PL arises from the excitonic core, with a peak at 462 nm, and the surface band with a peak at 565 nm. The core PL increases and blue-shifts as temperature is lowered. The surface PL increases in intensity more rapidly due to the relevant thermodynamics^{8, 11}



Figure 5.2 (a) Dual emission from a CdSe semiconductor nanocrystal. The size and chemical passivation was optimized for contrast over a wide temperature range. (b) The integrated area of the surface photoluminescence (PL) band relative to band edge exciton PL from the core of the nanocrystal. The points are data and the line is a polynomial fit. The inset shows the residual differences between the data and the fit. Reprinted with permission from Jethi et al., "Towards Ratiometric Nanothermometry via Intrinsic Dual Emission from Semiconductor Nanocrystals", J. Phys. Chem. Lett., 2015, 6 (4), pp 718–721. Copyright © 2015 American Chemical Society

Figure 5.2b shows the relative integrated areas of the surface band relative to the core band. This NC/ligand system shows a monotonic increase in the surface/core PL ratio as temperature is lowered. A simple 4th order polynomial fit provides a calibration curve. The sensitivity for optical ratiometric thermometry is defined as the change in photoluminescence (PL) ratio with change in temperature.

Therefore, internal sensitivity (S_{int}) is given as

$$S_{int}(T) = \left| \frac{d\left(\frac{Integrated Surface PL}{Total PL}\right)}{dT} \right|$$

The sensitivity range is ~ 0.69%K⁻¹ - 0.32%K⁻¹ with the maximum slope of 0.44%K⁻¹ which is comparable to previous studies over large range of temperatures below room temperature. The deviations from the fit are both small and random as shown in the inset.

As a portion of the emitted light arises from the surface^{8, 10-17}, it is essential to verify that this approach is sufficiently robust as to enable practical realization of optical thermometry via the intrinsic dual emission from NC. Historically, this broadened and red shifted PL was thought to arise from various defects, specifically at the surface of the NC. If the PL were to arise from some uncontrolled distribution of defects at the surface, creating a working device from surface emission would be impractical and unreproducible. Prior work from our group suggests that the surface PL may originate from a well-defined surface state that may be sufficiently robust with respect to processing as to enable reproducible device fabrication, whether light emitting diodes¹⁸ to the optical thermometer described here.



Figure 5.3 (a) Two different NC films from the same synthesis reveal similar temperature response. (b) The temperature response shows little to no hysteretic behavior. Reprinted with permission from Jethi et al., "Towards Ratiometric Nanothermometry via Intrinsic Dual Emission from Semiconductor Nanocrystals", J. Phys. Chem. Lett., 2015, 6 (4), pp 718–721. Copyright © 2015 American Chemical Society

Figure 5.3 shows the reproducibility and robustness of this system. Figure 5.3a shows the PL ratio for two different NC films as temperature sensors. Each film was made from the similar synthesis of NC (see section 2.5). Both films show identical temperature responses, demonstrating that the interface is robust with respect to processing into a working device. Figure 5.3b shows that there is also little to no hysteresis in the sensor.

Since NC are known to undergo aging which can degrade the PL due to assumed surface processes, these surface-based approaches must also be robust with respect to aging. Certainly, well passivated core/shell NC can be robust with respect to aging. But the behavior of the surface PL to aging is both unestablished, as well as likely to be pronounced by virtue of chemical contact to the environment. Aging studies for this system are shown in Figure 5.4. The figure shows the data from the same film before and after 30 days. After 30 days, the sensitivity is decreased with an increasing offset in surface to core ratio as the temperature is lowered. It is observed that the NC temperature sensor remains useable but with lower sensitivity.



Figure 5.4 Aging studies on sensor response. Reprinted with permission from Jethi et al., "Towards Ratiometric Nanothermometry via Intrinsic Dual Emission from Semiconductor Nanocrystals", J. Phys. Chem. Lett., 2015, 6 (4), pp 718– 721. Copyright © 2015 American Chemical Society

3.3 Conclusion

In conclusion, intrinsic dual emitting NC showing surface and core PL have been demonstrated for ratiometric temperature sensing in this chapter. These NC can be used in applications for large range of temperatures. They are robust and show little change with aging and reuse. Thus with further improvements, NC shown here can prove to be a potential candidate for studying various biological phenomenon using optical thermometric analysis as well as in thermal imaging.

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CHAPTER 6

Summary, Conclusions and Future Work

This thesis employs optical spectroscopy to study the properties of small, white light emitting NCs. The three articles published during the course of the PhD studies, emphasize on understanding the surface emission of NCs which can be potential candidate for device applications.

Chapter 3 shows the size dependent control of white light emission along with strong surface effects rationalized in terms of electron transfer theory. The transition from QD regime to molecular cluster regime in NCs was found to be around 1.2 nm radius.

Chapter 4 discussed the effect of thiols on small CdSe NCs surface properties. Fundamental properties such as stokes shift and PL intensities of phosphonate capped NCs were compared to thiol capped NCs. These studies were found to be consistent and suggested the origin of surface excitons to be from electrons bound to cadmium trap states. Chapter 5 eventually showed the application of small NC in nanothermometry. The dual emission bands of small NCs can be ratiometrically used for temperature sensing over a wide range of temperature. The sensitivity of such a sensor is comparable to reported values in literature.

Though discovered in 80's, the last decade has really been exciting for the nanocrystal community. As described in the first chapter, the NCs seem to be mature for certain display and lighting applications. One of the important issue for widespread adoption of CdSe NC is toxicity¹. Both cadmium and selenium are known to cause chronic and acute toxicities and are a major concern to the environment²⁻³. Moreover, cadmium is a probable carcinogen with a biological half-life of 15-20 years in humans¹. It bioaccumulates, can cross the blood–brain barrier and placenta, and is systemically distributed to all bodily tissues, with liver and kidney being target organs of toxicity. An in-depth toxicity study on Se contamination on the local environment by Hamilton³ describes a noticeable impact of Se on the local ecosystem.

Comprehensive toxicological data on NC is crucial for its acceptance in wide range of applications. The Restriction of Hazardous Substances (RoHS) guidelines make cadmium unsuitable for consumer devices. Although there is currently a temporary exception⁴ in effect to use cadmium in consumer devices approved by the European union, it is not clear how much growth will be seen for the technology, especially if intellectual property issues are limited through the expiration of the RoHS cadmium exemption.

Moreover, physical characterizing these small NCs is challenge. The contrast in TEM is weak and line broadening in XRD studies is severe. It is not only hard to describe the surface of NCs without proper characterization, but it also leads to irreproducibility with every slight variation surface chemistry and ligands. Sample preparation for every characterization techniques is the key to acquire better data. The post processing methods proposed in this thesis try to take a step further to improve upon getting better characterization data. Further, single molecule spectroscopy and low temperature (liquid helium) studies for such small NCs can provide insights on surface emission. It would confirm the vibrational structure of surface state, shedding more light on surface properties of small NCs and aid in developing a more sophisticated model to characterize the surface emission.

On more current technological and application aspects of NCs, this segment of the thesis will highlight some key advancements and future of NCs in displays. As described in chapter one, NCs have recently shown tremendous success commercially in displays to improve picture quality and efficiency. In future, it promises to bring several advancements in both, display and non-display applications. The current technology utilized NC in a film to enhance the color production in display devices⁵. The next step for NCs in displays is to be used as a replacement for color filters. Along with better color generation, it could provide higher efficiencies, brighter images as well as better viewing angles. The development of in-cell polarizers can make this happen as NCs depolarize light and currently, must be used after the polarizers in an LCD.

In the current display technology, the NCs are optically pumped. In future, the goal of NCs display is to be electrically pumped NC LEDs. Cadmium based NCs do perform in this area but with the increased focus on toxicity and emerging InP based NC devices the industry is moving on to improve efficiencies and device lifetimes.

Another technology which aims on reducing the cost of production of NC displays is Ink-Jet printing. Major companies like TCL with strong R&D in this sector have shown that printing NCs is becoming more and more viable.

The two major competitors to the existing NC display technology are the evolving Perovskite NCs and Micro-LEDs. The perovskite NC are now competing with both CdSe and InP NCs in the area of narrow emission and high absorbance for blue light. One of the concerns with these materials is that they are unstable. Stability improvements are expected in future as many research groups are working on improving these systems. The other major concern is the use of lead in perovskites which draws in the question of toxicity similar to Cadmium. The most recent and talked about technology for displays is a Micro-LED display. It uses a combination of micro RGB LEDs used for each pixel to achieve full color displays. Micro-LEDs could offer better contrast ratios, response times and energy efficiency. The main concern is the manufacturing process with the problem of mass transferring and bonding millions of LEDs to make an array for display. The accuracy of pick and place manufacturing technique is limited to pack the micro-LEDs.

That being said, NCs have come a long way since their inception and are still continuing to be one of the hottest topics for light generation application. Let's see what the future holds!

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APPENDIX A

Supplementary Information

A.1 Supplementary information for Chapter 3

Surface to total ratio (A_S/A_T) calculation using Marcus-Jortner ET theory:

The calculation is based on Marcus-Jortner electron transfer theory, in which the medium phonon modes were assumed to be negligible and set to zero (eq. 1).¹

$$W = Ae^{-S(2\bar{n}+1)}I_p(2S(\bar{n}(\bar{n}+1)^{\frac{1}{2}})[((\bar{n}+1))/(\bar{n})]^{\frac{p}{2}}$$
(1)

Where \bar{n} is the average phonon occupation number:

$$\bar{n} = \left(e^{\left(\frac{\hbar\omega}{kT}\right)-1}\right)^{-1} \tag{2}$$

And p is defined as:

$$p = \frac{\Delta G}{\hbar \omega} \tag{3}$$

 $I_p(x)$ is the modified Bessel function with imaginary arguments. The variables A is set as a rate constant, which is defined in Jortner's paper. S is the Huang-Rhys parameter.²

For the case of figure 3.4b in the article, the values of 25, 50 and 75 meV of ΔG were used, while all other parameters were held fixed. The Huang Rhys parameter was 20, and the constant A=10¹³. The value of ω is 208 cm⁻¹, which corresponds to the energy of the LO phonon for bulk CdSe.³ The forward and reverse rates were then calculated through detailed balance approach, in the same manner as previously described in the work of Mooney et al.⁴ The forward rate is defined here as W, whereas the reverse rate is $We^{\frac{\Delta G}{k_bT}}$. In this case the radiative lifetime of the core 1S state was set to be 20 ns (τ_r), and the radiative lifetime of the surface state is set to 200 ns (τ_{rS}), which are estimated based on TCSPC measurements. The following equations were solved using the *fsolve* function MATLAB® 2016a for the values of n₀, n₁, and n₂ which refer to the ground, core 1S and surface state respectively.

$$\frac{dn_0}{dt} = \frac{-n_0}{\tau_0} + \frac{n_1}{\tau_r} + \frac{n_2}{\tau_{rS}} = 0$$

$$\frac{dn_1}{dt} = \frac{n_0}{\tau_0} - \frac{n_1}{\tau_r} - n_1 W + n_2 W e^{\frac{\Delta G}{k_b T}} = 0$$

$$\frac{dn_2}{dt} = n_1 W - n_2 W e^{\frac{\Delta G}{k_b T}} - \frac{n_2}{\tau_{rS}} = 0$$

$$n_0 + n_1 + n_2 = 1$$

These populations are then related to their emission areas by scaling by their respective lifetimes and are plotted as a function of temperature.

$$A_{1S} = \frac{n_1}{\tau_r}$$
$$A_S = \frac{n_2}{\tau_{rS}}$$

...

Surface characteristics:

Figure S3.1 a and b show the size dependence on the FWHM and Stokes shift of the surface emission. A similar result is observed in the case of surface FWHM and Stokes shift where, larger NCs have smaller shifts and small NCs with larger shifts. As there is no observable surface emission at room temperature in larger NCs, this data only predicts the size dependence using peak fitting.



Figure S3.1 (a and b) Surface state FWHM and Stokes shift plotted as a function of radius, (c) Relation between surface FWHM and Stokes shift.

Figure S3.2 shows the energy shift between the core and surface photoluminescence emission as a function of radius. The energy shift approximately with a value of 120 meV from smaller NCs to larger NCs



Figure S3.2 Energy shift between Core and Surface PL emission as a function of radius.

To study the size dependent emission properties of NCs in colloidal solution and in polystyrene film, the data room temperature PL measurements for three different sized NCs as performed. Figure S3.3 shows the affect of ligands on the surface of NCs in both media.



Figure S3.3 PL spectra in solution and in polystyrene film for three diff radii (a and b)

In addition, Figure S3.4 shows the core fluorescence decay rate and atomic ratio characterization as a function of radius. Figure S3.4a shows time-correlated single photon counting (TCSPC) data where the decay rates are lower for ultra-

small NCs. The size dependent change in decay rates for ultra-small NCs can be attributed to the coupling of the core and surface states. Our results agree with a recent study showing similar lifetime data⁵.

The changes in the stoichiometric composition of NCs also strongly effect the optical properties such as the PL intensity and quantum yield.⁶⁻⁸ Energydispersive X-ray spectroscopy (EDX) data showing relative Cadmium to Selenium ratio is presented in Figure S3.4b. The NCs in the ultra-small regime show a higher cadmium content compared to larger samples. The smaller NCs are Cadmium rich which is in agreement with prior work ⁹. As the size increases the NCs are more likely to have a stoichiometric 1:1 Cd:Se ratio.¹⁰ Analogous results using Rutherford backscattering spectroscopy have previously been shown. ¹¹



Figure S3.4 a) Size dependent decay rates for smaller (blue) and larger (red) NCs showing the transition to molecular limit, b) Cadmium to selenium ratio for different sized NCs. Cadmium rich smaller NCs (blue) and larger NCs in red region

Figure S3.5 shows the PL quantum yields (QY) of the set of NCs with different sizes. The smaller sized NCs with large surface area show an increase in light emission and therefore larger QY.



Figure S3.5 PL QY for different sized NCs

Figure S3.6 shows the size dependent absorption data for NCs ranging 0.89 nm to 1.66 nm in radius. It can be noted that the larger NCs exhibit first and second excitonic peaks while the smaller NCs show only the first excitonic character.



Figure S3.6 Absorption spectra for different sized NCs

A.2 Supplementary information for Chapter 4

DFT Calculations

Table S4.1 Calculated Energy of the Highest Occupied Molecular Orbital (HOMO)by Density Functional Theory

Ligand	Our calculation (HOMO)	Literature Calculations (HOMO)	Literature Electron confinement volume
Thiophenol	-5.85 eV	-6.20 eV	154.70 A ³
ADMT	-6.12 eV	-6.40 eV	316;44 A ³
DDT	-6.24 eV	-6.50 eV	289.40 A ³

XPS Measurements

XPS sample preparation were done by suspending all quantum dots samples in Toluene. For XPS, P-doped silicon oxide wafers were cleaned with an AMI (Acetone, Methanol, Isopropanol) washing protocol and were dried under nitrogen. 150 μ L of the quantum dot suspension was drop-cast onto a wafer, and the wafer was dried under vacuum for 48 hours prior to XPS measurements.

XPS spectra were taken on a Thermo Scientific K-Alpha spectrometer (Al Ka). The X-ray spot size was 400 um2, and a low-energy electron flood gun was employed for charge neutralization. High resolution scans of the Cd and Se regions were taken using a 0.1 eV bandpass and analyser pass energy of 50 eV. Peaks areas were determined using the Thermo Scientific Avantage software.



Figure S4.1 XPS data for TOP capped dots



Figure S4.2 XPS data for ADMT capped dots



Figure S4. 3 XPS data for DDT capped dots

Temperature dependent data for Thiophenol (PhS):

PhS capped dual emitting QDs does not show any observable core peak (therefore most of analysis was not possible), however the surface is not quenched.



Figure S4. 4 a) Integrated Surface to core Ratio at different temperatures b) Temperature dependent PL spectrum for PhS capped QDs

A.3 Supplementary information for Chapter 5

Figure S5.1 shows the surface to core ratio for two different samples as a function of temperature. The aging effects on different samples are shown in figure S5.2 and S5.3 before and after 30 days of making the film.



Figure S5.1 Surface to core ratio for different samples



Figure S5. 2 Aging effect on sample 1



Figure S5.3 Aging effect on Sample 2

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