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Synthesis, Optical and Structural Characterization, and Exciton Dynamics of Doped ZnSe Nanocrystals and Simultaneous X-ray Emission Spectroscopy of Two Elements Using Energy Dispersive Spectrometer

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Synthesis, Optical and Structural Characterization, and Exciton Dynamics of Doped ZnSe Nanocrystals
and
Simultaneous X-ray Emission Spectroscopy of Two Elements Using Energy Dispersive Spectrometer

A dissertation submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

Sheraz Gul

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ABSTRACT

SYNTHESIS, OPTICAL AND STRUCTURAL CHARACTERIZATION, AND EXCITON DYNAMICS OF DOPED ZnSe NANOCRYSTALS AND SIMULTANEOUS X-RAY EMISSION SPECTROSCOPY OF TWO ELEMENTS USING ENERGY DISPERSIVE SPECTROMETER

BY
SHERAZ GUL

Doped semiconductor quantum dots (QDs) comprise an important subclass of nanomaterials in which a small quantity of impurity is added intentionally, adding another degree of freedom to alter their size-dependent physical and electronic properties. Intense, tunable, long lived and stable photoluminescence make them quintessential candidates for many opto-electronic applications including solid-state lighting, display devices and biomedical imaging. ZnSe QDs, which are blue-emitting fluorophores, were doped with Cu$^{+1}$ to redshift their photoluminescence (PL) to green region of the visible spectrum. These Cu-doped ZnSe QDs were then codoped with Al$^{3+}$, Ga$^{3+}$ and In$^{3+}$ to improve the PL quantum yield (QY) by eliminating the defect states originating from charge imbalance created by aliovalent doping. Codoping also resulted in further redshifting of the PL, covering most of the visible spectrum, making them potential candidates for use in solid-state lighting and as optical down converters in next generation light emitting diodes (LEDs). To better understand the optical properties of these materials, local structure around the luminescent centers was investigated by extended X-ray absorption fine structure (EXAFS). Cu was found to occupy a distorted tetrahedral site with the codopant residing in a substitutional Zn site. Based on the structural information obtained by EXAFS, density functional
theory calculations (DFT) were performed to get a clear picture of the energy levels associated with the electronic transitions. Furthermore, the dynamics studies of the exciton and charge carriers were carried out to get deeper insight of the various photophysical processes involved. The fluorescence lifetime was increased approximately 10 times after doping.

The multielectron catalytic reactions often involve multimetallic clusters, where the reaction is controlled by the electronic and spin coupling between metals and ligands to facilitate charge transfer, bond formation/breaking, substrate binding, and release of products. A method was developed to detect X-ray emission signal from multiple elements simultaneously to probe the electronic structure and sequential chemistry that occurs between the elements. A wavelength dispersive spectrometer based on the von-Hamos geometry was used, that disperses Kβ emission signals of multiple elements onto an area detector, and enables an XES spectrum to be measured in a single-shot mode. This overcomes the scanning needs of the Rowland circle spectrometers, and the data is free from temporal and normalization errors, and therefore ideal to follow sequential chemistry at multiple sites. This method was applied to MnOx based electrocatalysts, and the effect of Ni addition was investigated. Electro-deposited Mn oxide catalyses oxygen-evolution reaction (OER) and oxygen-reduction reaction (ORR) at different electrochemical potentials under alkaline condition. Incorporation of Ni reduced the low valent Mn component resulting in higher average oxidation state of Mn in MnNiOx under ORR and OER
conditions, when compared to MnO\textsubscript{x} under similar conditions. The reversibility of the electrocatalyst was also found to improve by the inclusion of Ni.
Dedication

I dedicate this work to my mother whose support and prayers have made this possible. No words in any language can express the gratitude for what she means to me.

And to my Wife

Her love and support are the source of inspiration for me. I couldn’t have asked for a better partner and friend.
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The text of this dissertation includes reprints of the following previously published material:


CHAPTER 1: Synthesis Optical and Structural Properties, and Charge Carrier Dynamics of Cu-doped ZnSe Nanocrystals

1.1 Abstract

Stable and luminescent Cu-doped ZnSe nanocrystals (NCs) were synthesized in organic solvents with octadecylamine (ODA) as the capping ligand, and characterized using a combination of optical and structural characterization techniques. Successful doping was achieved by adding Cu during the growth phase of the NCs when their size was approximately 4 nm. The appearance of red-shifted, intense photoluminescence (PL) peak with doping indicates the incorporation of Cu in the NCs and stability of dopant emission infers the internal doping of NCs. Extended X-ray absorption fine structure (EXAFS) studies revealed that Cu is surrounded by four neighbors in the lattice but is very close to the NC surface and gets oxidized when NCs are precipitated from the solution. For the undoped sample, time-resolved PL studies using time-correlated single photon counting (TCSPC) reveal the luminescence decay lifetimes of about 1.1 ns, 12 ns and 60 ns that we attribute to near bandedge, shallow trap (ST) state, and deep trap (DT) state emissions, respectively. In addition to these decay components, the Cu doped sample was found to have a long-lived component with a lifetime of 630 ns. Luminescence decay lifetimes of near bandedge and ST state emissions were slightly shortened by doping (1 and 10 ns respectively), suggesting that the Cu dopant competes with these states in trapping the charge carriers from the conduction band (CB) or near bandedge states. However, the presence of Cu was found to increases the lifetime of DT states from 60
ns to 100 ns probably due to a decrease in coupling of electron and hole states involved in this emission upon Cu doping. Synthesis of such stable, doped samples along with a better understanding of charge carrier dynamics is significant for emerging optical applications of these NCs.

1.2 Introduction

Luminescent semiconductor nanocrystals (NCs) or quantum dots (QDs) have stimulated a great deal of research interest owing to their fundamentally intriguing properties resulting from quantum confinement effects and large surface-to-volume ratio,[1-9] along with their potential applications in areas including biomedical labeling, photovoltaics, and light emitting diodes.[10-15] Their properties can be varied in a controllable manner by varying size, shape, and surface functionalization.

In particular, CdSe QDs have been studied extensively due to their absorption and emission wavelength ranges spanning much of the visible spectrum. However, the inborn toxicity of cadmium has rendered the CdSe QDs less useful, regardless of their obvious advantages.[16, 17] Wide bandgap semiconductor NCs doped with transition metal ions have developed as promising alternatives with tunable emission spanning the visible as well as near IR spectral window. Incorporation of small amount of dopant impurity changes the optical, magnetic and electronic properties of host semiconductor QDs.[18-25] Some of the unique characteristics attributed this subgroup of nanomaterials include longer excited state lifetime, minimum self absorption, broad emission spectral window and thermal stability.[25-28] These transition metal ion doped semiconductor NCs, such as zinc chalcogenides, can be a
good alternative to the more toxic NCs to the emerging field of NC based devices but due to the extremely small volume of the NCs and dynamic nature of growth process, doping all the NCs concurrently has been an issue to be tackled, even with powerful organometallic methods.[28-30]

In the case of ZnSe, Mn-doped NCs have been studied extensively and successfully which show stability and efficient photoluminescence ranging from 580 to 600 nm.\textsuperscript{[10, 31, 32]} Due to similar crystal structure (zinc blende) and comparable lattice parameters of MnSe, Mn can be easily incorporated into ZnSe. However, doped NCs emitting in other regions of visible spectrum are required for some applications. Doping semiconductor NCs with Cu provide one option to fulfill this requirement, but contrary to Mn doping, serious problems have been encountered in the case of Cu doping because of different crystal structure of copper selenide. Though some progress has been made in the recent years regarding Cu doing in this system,\textsuperscript{[25, 33, 34]} the mechanism of Cu doping into the NCs, the nature of the Cu dopant related emission, local structure around the dopant, and photochemical stability of the Cu-doped NCs are still unresolved issues that require further study.

Studies of charge carrier dynamics using time resolved fluorescence measurements not only provide information about the nature of the optical transitions but also give insight into the local environment around the optically active species and provide information about how charge carriers interact with phonons and particle surface.\textsuperscript{[35, 36]} In addition, it is highly desirable to study the lifetimes of various decay processes involved in photoluminescence (PL) for improving device
performance in applications of NCs, such as display devices, sensors, quantum cryptography, solar cells and lasers utilizing these NCs.[1, 37-40] Charge carrier dynamics studies in semiconductor NCs has proven extremely powerful in understanding fundamental properties of the particles’ electronic structure which are crucially important in device applications. For instance, at the fundamental level, it is interesting to explore how the quantum confinement effects would alter the luminescent properties of dopant ions in semiconductor NCs as increase in energy level spacing has drastic effects on the rates at which excess electronic energy of an electron or hole dissipates.[13, 41-43] Another factor affecting the charge carrier dynamics in NCs is the surface of particles. NCs have large percentage of surface atoms often giving rise to surface dangling bonds and defects. Such surface defects and dangling bonds can introduce states within the bandgap of semiconductor that can strongly affect relaxation pathways of charge carriers.[44-46] Luminescence decay kinetics of Mn$^{2+}$ doped samples has been studied extensively [47-49] but such detailed studies of Cu-doped ZnSe are scarce and warrant further investigation.

In this work, we seek to gain some new insights regarding the doping parameters and stability of ZnSe:Cu NCs that were sufficiently stable against photo-oxidation and exhibited PL quantum yield up to 3-8% even after months. It was observed that the choice of the alkyl phosphine used to dissolve Se and the particle size at which the dopant precursor is added are very important parameters for successful doping which requires the impurity ion to bind strongly to the surface of the host particle. As Cu ions bind strongly to only certain facets of the host NC,[29]
the dopant precursor should be added when the host NCs have well defined crystal facets which are achieved only after the particle has grown to larger sizes. The host nuclei with particle size around 4 nm are large enough to exhibit polyhedral morphology, at which point the dopant ions adsorb onto the NCs strongly enough to stay within the host lattice upon further growth, thereby achieving successful doping. NCs that were sufficiently stable against photo-oxidation and exhibited PL quantum yield up to 3% even after months were synthesized using this technique.

Furthermore, a detailed study on exciton recombination dynamics of NCs has been carried out using time correlated single photon counting (TCSPC). A multi exponential fit to the decay traces of undoped ZnSe sample yielded lifetimes ranging from a few ns to tens of ns, that have been attributed to near bandedge and trap state emissions. Upon doping with Cu a new long lived component of 630 ns appeared in addition to those observed in case of undoped NCs, which has been attributed to the transition involving Cu specifically. Kinetics of near bandedge and ST emissions was affected slightly by Cu doping resulting in shortening of their lifetimes. However, incorporation of Cu significantly affects the decay rate of DT state emission. Our findings are not only important in improving the synthesis of doped semiconductor NCs in general but also provide new insights into the charge carrier dynamics of Cu-doped ZnSe NCs specifically.
1.3 Experimental Methods

1.3.1 Materials

Octadecene (ODE, 90%), zinc stearate (technical grade), tri-n-butylphosphine (TnBP, 99%), tributylphosphine (TBP 97%, mixture of isomers), copper acetate (98%), Octadecylamine (ODA, 99%) Copper Acetate (99.9%) and chloroform (99.9%) were purchased from Sigma-Aldrich. Anhydrous zinc acetate (99.98%) and Se powder (<325 mesh, 99.7%) were from Alfa Aesar and Acros Organics, respectively. Methanol (99.9%), Acetone (99.7%), and Hexanes (99.8%) were purchased from Fisher Scientific. All the chemicals were used without further purification.

1.3.2 Synthesis of Cu-doped ZnSe NCs

Copper doped ZnSe QDs were synthesized using growth doping method similar to the one used by Peng et al.,[25] with some modification. In a typical synthesis, 0.06 g zinc stearate and 10 ml ODE were loaded in a 50 ml three-neck flask which was then connected to Schlenk line. The mixture was evacuated up to 100 mmHg three times at room temperature and once at 90 °C for 10 minutes each and then, under argon flow, temperature was raised to 300 °C. 0.040 g Se powder was dissolved in 0.40 g TBP along with 0.15 g ODA in a glove box and 1 ml ODE was added to this solution. This Se solution was injected to the reaction mixture at 300 °C and was cooled down to 250 °C for growth. To monitor the size of the NCs using UV-Visible spectroscopy, small aliquots (~0.2 ml) were taken from the flask with a syringe and diluted to an optical density between 0.2 and 0.3 using chloroform. When
the desired particle size was reached, temperature was lowered to 200 °C and calculated amount of copper acetate stock solution was added that was prepared by dissolving 1.074 x 10^{-3} g copper acetate in 1.25 g TBP. Temperature was then slowly ramped up to 220 °C and maintained for two hours. At this temperature slow growth continues along with the doping. To build the ZnSe shell, small amounts of 0.05 M zinc acetate solution (0.15 ml) in TBP and ODE (0.1 M solution in TBP diluted to 0.05 M with ODE) were added drop-wise at regular intervals at 230 °C until stable, internally doped NCs were made as indicated by the stability of PL. To avoid broader size distribution during growth, zinc and selenium solutions were added at regular intervals[50] except during the doping process. Undoped sample was prepared under the same conditions.

1.3.3 Purification of NCs

As-prepared NCs in ODE were mixed up with an equal volume mixture of hexanes and methanol (1:3, v/v) by shaking vigorously and then centrifuged to get the methanol phase separated. Methanol layer was discarded and the process was repeated two to three times. With repeated extractions the amount of ODE gradually decreased and that of hexanes increased with NCs being fairly soluble in this phase. To get the solid particles, after a couple of extractions, the NCs in ODE phase were precipitated using minimum amount of acetone and recovered by centrifuging. As observed by others,[51] crashing the particles results in significant loss of PL regardless of the sample being doped or undoped. Therefore, except for XRD, ICP and EXAFS measurements the NCs were stored in hexanes and ODE phase obtained
after repeated extractions. In this phase NCs did not show any significant loss of PL even after months.

### 1.3.4 Instrumentation

The UV-Visible spectra were recorded at room temperature using Hewlett Packard 8452A diode array spectrometer. Perkin-Elmer Luminescence spectrometer LS50B was used to obtain the PL and PL excitation spectra at room temperature. Low-resolution TEM measurements were performed on a JEOL model JEM-1200EX microscope at 800KV. High-resolution TEM was performed on a Philips CM300-FEG at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory.

Cu concentrations were determined through inductively coupled plasma (ICP) measurements using a Perkin-Elmer Optima 4300DV inductively coupled plasma optical emission spectrometer (ICPOES). NCs were repeatedly purified to remove excess precursors and then dispersed in chloroform. After evaporating the chloroform, dried samples were digested in concentrated nitric acid, and pumped at a rate of 1.5 mL/min into the plasma chamber. For EPR measurements, a Bruker ElexSys E500 (9.5 GHz) spectrometer, equipped with a standard TE$_{102}$ cavity, was used. Data was collected at ~115-125 K using a variable temperature control system equipped with a nitrogen vapor using cavity.

X-ray diffraction (XRD) measurements were performed on a Rigaku Americas Miniflex Plus powder diffractometer using Cu K$_\alpha$ ($\lambda = 1.5405$ Å) as the incident radiation. Diffraction patterns were recorded at a rate of 2° per minute with a
step size of 0.04°. Sorvall RC-5C Plus centrifuge was used at 14000 rpm at room temperature to crash the NCs. FTIR measurements were carried out with a Perkin-Elmer FTIR spectrometer (spectral resolution 4 cm\(^{-1}\)).

For the EXAFS studies, ZnSe:Cu nanocrystals were deposited on a filter paper, and then encapsulated in tape; a single layer of this kind was used in the data collection process. The EXAFS data were collected at the Stanford Synchrotron Radiation Light source (SSRL), on beamline 10-2 at 10 K, using a Si (111) double monochromator, detuned 50% at 9200 eV to reduce harmonics. Small slits with a height of ~0.7 mm gave an energy resolution of 1.3 eV. The Cu K-edge data were collected in fluorescence mode, using a 13-element Ge fluorescence detector, and were reduced using standard techniques (RSXAP).[52]

Lifetime studies of the ZnSe doped and undoped systems were performed at room temperature using TCSPC. A 5 W Coherent Verdi-V5 (532 nm) laser was used to excite a Ti:sapphire crystal within an optical resonator cavity (Kapteyn-Murnane Laboratories, Model: MTS Mini Ti:Saphire) to produce a tunable mode locked laser line between 790-820 nm with a frequency of 200 MHz and average power of 333 mW. The mode locked light source was passed through a pulse picker (Conoptics, Model 350-160) controlled by a Conoptics synchronous countdown (model 305) allowing for the pulse train to be set to durations ranging from 50 to 2600 ns. The pulse picked light (790 nm) was then frequency doubled by passing it through a BBO crystal which was subsequently reflected of a dichroic mirror which was passed through a quarter wave plate and polarizer. This beam was then incident upon the
sample at which point the beam width was 2 mm. Photo-generated emission was collected at 90° with respect to the pump laser with a series of collector and focusing lenses and mirrors which guided and concentrated the signal through a 420 nm cutoff filter, to remove laser light, and a magic angle polarizer before it was separated by a monochromator (Princeton Instruments SP2150i) with 0.25 nm resolution with 1200 groves/mm and 500 nm blaze grating. The monochromatic light was focused on an avalanche photodiode (id-Quantique id100-50 single photon detection module) whose signal was recorded with a photon counting board (Becker and Hickl GmbH, Model: SPC 630) which collected in reverse stop-start mode.[53]

A number of time windows were collected to adequately characterize the wide range of time constants observed in the decay spectrum of the samples investigated, and were 50, 380, and 2000 ns for individual emission wavelengths ranging from 430 to 560 nm which were recorded every 10 nm. The undoped ZnSe QDs were probed using a 50 ns window over 4096 channels, a 380 and 1000 ns window over 1024 channels using repetition rates which allowed the particles to fully recover for the various components measured. For the Cu-doped sample we monitored the following time windows over the reported channels: 50 ns/4096, 380 ns/1024, 2000 ns/256 channels. The instrumental resolutions were 0.05, 0.32 and 0.7 ns for 50, 380 and 2000 ns time windows respectively. Data was analyzed using an IGOR Pro-based (wavemetrics) macro procedure developed in-house.
1.4 Results and Discussion

1.4.1 Effect of Alkyl Phosphines on Nanocrystal Growth

Monomer activity defined as the effective monomer concentration plays a key role in NC synthesis and is profoundly affected by the ligands.[54] Alkyl phosphines are used to dissolve Se and the concentration, steric effects and length of the alkyl chain determine the effects of alkyl phosphines on monomer reactivity. The monomer reactivity decreases with increase in ligand concentration and the strength of the bond between the monomer and ligand.[55, 56] In case of alkyl phosphines with the same number of carbon atoms, greater monomer activity was observed for those having greater steric hindrance due to alkyl chain branching. In case of 99.9% TnBP, beyond a certain concentration (~0.5 M), the monomer phase is so stable that nucleation does not happen. However, starting with lower concentration of TnBP, nucleation does happen, but as the concentration of TnBP increases, while adding zinc acetate solution in TnBP, the particles finally disintegrate. When using Tri-isobutylphosphine (TiBP) or mixture of isomers in which case the bonding strength to the monomer is the same as that of TnBP but owing to greater steric factor, the monomer activity is greatly enhanced, which results in better yield of NCs. Also, the NCs are found to be fairly stable at higher concentrations in the case of TiBP and mixture of isomers. This could be due to the fact that during dynamic growth of the NCs, once incorporated into the NC it is hard for the free bulky ligand to get attached to the anion and have it back into the monomer phase.
1.4.2 Effect of Cu-doping on ZnSe NCs

Synthesis of transition metal doped II-VI semiconductor NCs has proved to be challenging. The obstacles have been reported to be due to intrinsic “self-purification” property of QDs whereby dopants are expelled to the surface,[57, 58] leading to PL quenching. However, a kinetics-based model for successful doping of semiconductor NCs has been proposed by Erwin et al.[29] Based on this model, adsorption strength of doping impurities on well-defined nanocrystal facets determines the doping, and binding energies of dopants are higher for Se rich (001) facets of zinc blende structure as compared to the other crystal facets. The surface composition of the NCs can be controlled by the relative concentrations of its constituents during the nucleation and growth process. Therefore, carrying out the growth in Se rich medium makes it possible to get NCs with Se rich facets on the surface. As a result, all the syntheses in this investigation were started with a Se:Zn ratio of 6:1. Since such well-defined facets develop after the NCs have grown up to a certain diameter at which stage the NCs exhibit polyhedral morphology,[59] the Cu doping precursor was added after the particle size reached around 4 nm, corresponding to an exciton peak position around 400 nm as monitored by UV-visible absorption. Even if the dopant was added at early stage of growth, no stable PL was observed until the particle size had grown bigger enough to demonstrate polyhedral morphology. Also, increasing the temperature beyond 240 °C, during or after the doping stage to enhance growth rate, results in completely surface doped NCs whose PL quenches quickly. Since more active zinc precursor, that is, zinc acetate dissolved in TBP, is required for growth at
lower temperature, NCs were allowed to grow up to ~4 nm at higher temperature using zinc stearate as the zinc source. This would reduce the amount of TBP required for zinc acetate solution that has to be used for growth after the addition of dopant precursor.

1.4.3 Structure and Composition: XRD, TEM and ICP

Figure 1.1 (a) shows the representative XRD pattern of the sample indicating a zinc blende structure. (111), (220) and (311) diffraction peaks are seen in the XRD pattern. The signal has some background from the glass substrate on which the sample was mounted. The peak broadening is an indicative of the nanocrystalline nature of sample. From the line width of (111) peak, the average crystallite size was calculated to be around 6 nm using the Debye Scherrer formula.[60] From the TEM image of ZnSe:Cu_{0.5\%} sample, diameters of 150 particles were measured using the ImageJ program (distributed by NIH) and average particle size was found to be around 6 nm with a size distribution of ~10\% (Figure 1.1 b). HRTEM image of single nanocrystal in the inset clearly infers the crystalline nature of quantum dots.

ICP measurements were performed on doped samples with varying Cu concentrations. The results showed an incorporation efficiency of almost unity with respect to the zinc incorporated. Quantitatively, this might seem a little bit higher than expected but, qualitatively, these results are in agreement with observed PL attributed to Cu doping and comparable results (with 10\% error) were seen from the ratios of step heights of Cu and Zn K-edges during EXAFS measurements.
1.4.4 Structural Characterization: EXAFS

An average of four $k$-space data scans for the ZnSe:Cu$_{0.6\%}$ sample is shown in Figure 1.2 (a) and shows a reasonable signal-to-noise ratio out to $\sim$10Å$^{-1}$; for the ZnSe:Cu$_{0.1\%}$ sample, the overall amplitude is larger and the signal-to-noise ratio is better. Figure 1.2 (b) shows the $r$-space data obtained using a Fast Fourier Transform (FFT) $k$-range of 3.0–9.5 Å$^{-1}$ for two samples, ZnSe:Cu$_{0.1\%}$ (top panel) and ZnSe:Cu$_{0.6\%}$ (bottom panel). The peaks in $r$-space correspond to shells of neighbors at different distances from the excited Cu atom. These peaks are shifted by a known amount (roughly -0.3 Å) compared to actual bond lengths.

The data in Figure 1.2 (b) shows a prominent peak near 1.6 Å, but in ZnSe:Cu, the first Cu-Se peak for Cu on the Zn site, should occur farther out, near 2.1
Å, assuming little distortion. Thus an apparent shortening by ~0.5 Å is unexpected, and inconsistent with simple substitution. However, in CuO, Cu has four O neighbors in the first shell with almost equal bond lengths; two at 1.95 Å and two at 1.96 Å, and in r-space these peaks occur near 1.6 Å. Thus, a visual examination of the r-space data suggests that a significant amount of oxygen has been introduced into the Cu environment in the ZnSe:Cu NCs. Theoretical Cu-O and Cu-Se single-peak EXAFS functions were generated using the known crystal structures and the FEFF8.2 code. [61] Fitting the data to a sum of these two peaks (Figure 1.2b - dots), with the total amplitude constrained to 4 neighbors and the amplitude ratio of Cu-O to Cu-Se allowed to vary, yielded a good fit.

**Figure 1.2:** (a) An average of four data scans for the ZnSe:Cu$_{0.6\%}$ sample in k-space. The data for the ZnSe:Cu$_{0.1\%}$ (not shown) have a larger amplitude and a higher signal to noise ratio. (b) Averaged r-space data (solid black line), fit of data to theoretical Cu-O and Cu-Se peaks (blue dots), single Cu-O peak (red line), and single Cu-Se peak (dotted magenta line) for ZnSe:Cu$_{0.1\%}$ (Top Panel) and ZnSe:Cu$_{0.6\%}$ (Bottom Panel). For the ZnSe:Cu$_{0.6\%}$, N1=2.060, N2=1.940, $\sigma_1=0.0799$, $\sigma_2=0.1049$. For the ZnSe:Cu$_{0.1\%}$, N1=3.116, N2=0.884, $\sigma_1=0.0952$, and $\sigma_2=0.0920$. 
for both samples. In both cases the Cu-O amplitude was large. In these fits the Cu-O and Cu-Se bond lengths were also allowed to vary but did not change by more than 0.01 Å, confirming the presence of oxygen in the NCs. For the ZnSe:Cu<sub>0.1%</sub> sample, the Cu-O to Cu-Se amplitude ratio is roughly 3:1, while for ZnSe:Cu<sub>0.6%</sub> the amplitude ratio is closer to 1:1, indicating a smaller relative amount of oxygen.

Since the PL of surface doped NCs gets quenched within a few minutes,[25, 33] we assume that Cu was initially present within the host NCs as PL did not show any significant decrease over a period of months if particles were not precipitated, even with a shell that was about 1 nm thick. As indicated by the PL loss along with decreased solubility, crashing the NCs from solution results in considerable loss of capping ligands which leads to surface oxidation and corrosion of NCs as observed in CdSe[62] where exposure to air resulted in diffusion of oxygen to deeper layers after oxidizing the surface Se. Also, the sample which shows greater Cu-O to Cu-Se amplitude ratio (3:1) was precipitated five times and suffered more loss of capping ligands as compared to the second sample that was crashed only twice and exhibited the Cu-O to Cu-Se amplitude ratio of approximately 1:1. Alternatively it can be argued that at lower concentrations Cu was mostly present on the surface as reported in case of Mn-doped ZnSe[63] and Cu-doped ZnS[64], but it requires further EXAFS investigations of the ZnSe:Cu samples in solution form before precipitating.

1.4.5 FTIR Analysis of Surface Ligands

Identification of the capping ligands attached to the sample after washing was achieved through use of FT-IR. Briefly, a small amount of QDs dispersed in hexanes
was deposited on a NaCl window and allowed to dry under N$_2$(g) stream upon which the disk was placed in the vacuum transfer chamber of a nitrogen glove box and evacuated for 10 minutes. The chamber was filled with N$_2$(g) and the disk was transferred to a desiccators and stored for no more than one hour before the spectrum was collected. The resulting spectra were characteristic of an aliphatic primary amine indicated by the stretching frequencies: 1555 cm$^{-1}$ (NH$_2$ scissoring), 1466 cm$^{-1}$ and 1377 cm$^{-1}$ (CH$_2$ bending), 1076 cm$^{-1}$ (CN stretching), shoulder 738 cm$^{-1}$ (NH$_2$ out-of-plane bending), and 721 cm$^{-1}$ (CH$_2$ rocking).[65] To verify the identity of the ligands, spectrum was recorded using a sample prepared with free ODA in KBr. Both spectra have been reported in Figure 1.3 over the range from 600-1800 cm$^{-1}$ as the NH stretching region was not useful in identification due to broadening effects and have therefore not been reported. A quick comparison of the two spectra further confirms the identity of the capping ligand as a long chain aliphatic primary amine.

**Figure 1.3:** FT-IR spectra of ZnSe:Cu capped with octadecylamine as a thin film on a NaCl window (red) and octadecylamine (green) for comparative identification.
1.4.6 Oxidation State of Copper

Though the precursors used for doping semiconductor NCs with Cu contain Cu(II), literature regarding the oxidation state of Cu in the resulting NCs is inconsistent. While some have reported the existence of Cu(II),[33, 34, 66, 67] others have argued about its incorporation as Cu(I).[64, 68-71] Since Cu(II) is a $d^9$ system with one unpaired electron and Cu(I) being $d^{10}$ system is diamagnetic, the EPR spectra of doped samples with different Cu amounts were taken to confirm the oxidation state of Cu within our NCs. None of the samples exhibited any detectable EPR signal (Figure 1.4), indicating the presence of copper as Cu(I). This is in agreement with earlier reports where no EPR signal was detected for Cu-doped semiconductor NCs, except under excitation where paramagnetism has been observed.[72] Therefore, we believe that

![Figure 1.4: EPR spectra of ZnSe:Cu_{0.5%} and reference copper acetate sample.](image)

NCs. None of the samples exhibited any detectable EPR signal (Figure 1.4), indicating the presence of copper as Cu(I). This is in agreement with earlier reports where no EPR signal was detected for Cu-doped semiconductor NCs, except under excitation where paramagnetism has been observed.[72] Therefore, we believe that
Cu(II) was reduced to Cu(I) in the reaction medium as reported by Isarov et al., who have proposed the reduction of Cu(II) to Cu(I) by anions constituting the NCs.[69]

1.4.7 UV-Visible Absorption Spectra

Successive UV-Visible spectra for ZnSe:Cu$_{0.7\%}$ sample are shown in Figure 1.5. Given the bandgap of the bulk material being 2.69 eV (461 nm) and Bohr exciton radius of 4.5 nm,[73] the first excitonic transition at 2.99 eV (415 nm) observed in the UV-visible spectra is clearly blue shifted and indicative of quantum confinement. After TBPSe injection, the initial growth was rapid and, within a few seconds, the first excitonic peak appeared around 380 nm, indicating the formation of NCs. Initially, the excitonic peak was broad due to a broad size distribution. But, as the growth continued, the spectra evolved into narrower peaks, suggesting nearly monodisperse size distribution of NCs. Undoped and doped ZnSe NCs showed indistinguishable UV-Vis spectra(Figure 1.6), indicating that Cu doping has no or negligible effect on the electronic absorption of the host ZnSe NCs.

**Figure 1.5:** UV-visible spectra of ZnSe:Cu$_{0.7\%}$ sample at different time intervals.
1.4.8 Photoluminescence

1.4.8.1 Undoped ZnSe NCs

To better understand the relevant energy levels in doped and undoped NCs, it is useful to briefly review the properties of the corresponding bulk system. Bulk ZnSe with a bandgap of 2.69 eV (461 nm) exhibits bandedge emission around 2.67 eV (465 nm) along with the self activated emission involving a donor-acceptor pair (DAP).[74, 75] Donor-acceptor nature of this process has been confirmed through optically detected magnetic resonance (ODMR) and time resolve spectroscopy.[75-77] Intrinsic defects like interstitial zinc or halides that are not detectable in spectroscopic analysis, could be the donors involved in self activated emission. Recently, oxygen as an unavoidable background impurity has been reported as the donor impurity involved in self activated emission.[78] These donor centers have been reported to

![Figure 1.6: UV-Visible absorption spectra of an undoped (red) and a representative doped sample (green).](image)

20
exist 0.01-0.03 eV below the conduction band (CB) as determined by measurements of Hall coefficients of bulk samples.[79-81]

Figure 1.7: PL and PL excitation spectra of undoped and Cu-doped ZnSe NCs. Inset: PL spectrum of undoped sample along with the three peaks generated through fitting.

Figure 1.8: Proposed energy level diagram for doped and undoped sample. The blue emission at 435 nm (2.85 eV) and green Cu emission at 515 nm (2.4 eV) have been described as originating from defect and impurity-induced ST states just below the CB.
PL spectrum of undoped NC sample synthesized under the same conditions as a doped sample and excited at 390 nm is shown in Figure 1.7. The near bandedge emission peak around 435 nm (2.85 eV) is asymmetric and fitting reveals that it consists of two Gaussians, one peaked at 433 nm with a FWHM of 15 nm and the second one peaked at 445 nm with a FWHM of 20 nm. This might arise due to transitions involving impurity donors and ST states respectively. The fitting is shown in the inset of Figure 1.7. In addition to this main band, the PL spectrum features a broad low intensity band with a maximum around 478 nm (2.6 eV), as determined by the fitting. This broad band is attributed to emission from DT states and self activated emission comprising DAP recombination involving impurity donors and acceptors like Zn vacancies or zinc vacancy-donor associated pairs on neighboring sites, as the sample was synthesized in Se rich medium.

Figure 1.9: Normalized PL spectra before and after the addition of dopant precursor along the course of synthesis for ZnSe:Cu$_{0.7\%}$. Dopant precursor was added after the host particles have grown for half an hour. $\lambda_{ex} = 335$ nm when particles are really small (30 Sec and 15 min spectra) and $\lambda_{ex} = 390$ nm afterwards.
Near bandedge emission arises from the initial excitation of valence band (VB) electron to CB from where it descends to the ST states or impurity donors and then recombines with the hole in CB or hole trap states, resulting in the emission around 435 nm. DT state emission stems from zinc vacancies or selenium dangling bonds on the surface, giving rise to states deep in the bandgap of the ZnSe NCs.[82, 83] Here, the photogenerated hole is immediately filled by an electron from the selenium atom with dangling bond. Subsequent emission follows after the hole migrates and finally recombines with the electron in the CB or vice versa. This emission is always broad since there would be many different selenium dangling bond species on the surface that might be singly or doubly filled. Fit generates the broad featureless region that peaks around 478 nm (Figure 1.7). A schematic energy level diagram describing all the decay processes is shown in Figure 1.8.

1.4.8.2 Cu-doped ZnSe NCs

The spectral evolution of the PL of doped sample is shown in Figure 1.9. The PL spectra are similar to those observed by others previously.[25, 33] The dopant precursor was not added until the host NCs had grown to a certain size (~4 nm), where they exhibit polyhedral morphology at which stage the PL peak was around 415 nm. After adding the
dopant precursor, the host peak started to decrease in intensity while the contaminant peak increased. Complete doping took about two hours during which time slow growth was also observed as indicated by the movement of bandedge absorption along with a redshift of the emission band.

As long as Cu ions were on the surface, the PL would decrease sharply in a few seconds; but once the host shell was grown, the PL became stable and was found to increase with time if the sample was kept under a UV light, due to photo-annealing. A digital photograph along with the corresponding PL spectra of undoped and doped ZnSe NCs, with different concentrations of Cu, under UV irradiation, is shown in Figure 1.10 signifying the greener emission with increasing Cu amount.
With Cu-doped bulk samples, two Cu acceptor centers have been reported, one 0.7 eV above the VB involved in Cu-red emission and another 0.4 eV above the VB giving rise to Cu-green emission.\cite{76, 77, 84} In the PL spectra of the NCs the energy difference between the maxima of near bandedge and dopant emission was found to be about 0.4 eV. This energy difference puts the Cu level 0.4 eV above the VB (Figure 1.8), indicating that the Cu emission in ZnSe:Cu NCs is analogous to the Cu green emission in the bulk material. Due to quantum confinement effects, the CB moves to higher energies, resulting in blue shifting of the green emission with decreasing particle size.

A proposed mechanism of the observed emission involves the initial excitation of a VB electron to the CB in the host ZnSe. Cu(I) ion being negatively charged with respect to the lattice then binds the hole through long range coulomb interaction in an effective mass-like state, producing a transient Cu$^{2+}$ acceptor state. This process involves a transition from undistorted Cu$^{+}$ to Jahn-Teller distorted Cu$^{2+}$ ion, but lattice strain during this transition is not taken into account because when Cu is substituted into a tetrahedral lattice site, Jahn-Teller effect has to work against the forces maintaining the lattice and distortion is expected to be minimized. Next, the electron in the CB moves to a ST state associated with zinc dangling bonds or impurity donors such as halides or associated oxygen, as observed in EXAFS analysis, from whereon follows the recombination of this electron with the hole trapped d-state of Cu. This donor-acceptor recombination results in emission at 515 nm (2.4 eV).
Transient Cu\textsuperscript{2+} state is split into higher \( t \) and lower \( e \) levels (Figure 1.8) giving rise to \(^2T_2\) (\(^2D\)) ground state or \(^2E\) excited state and both of these have the possibility to accept excited electron, which results in broadening of the dopant peak\[71, 85, 86]\ that has a FWHM of about 80 nm. The positions of neither excitonic nor the dopant emission band show any change with excitation wavelengths between 335 to 390 nm. Also, the PL excitation spectra recorded for different emission wavelengths were found to be similar. This further supports the view that broadness of emission is intrinsic and not due to heterogeneity of NCs in terms particle size distribution. During the two hour doping process, no zinc precursor was added that resulted in broader particle size distribution but addition of zinc precursor during shell growth was found to make the size distribution narrower resulting in the reduction of FWHM of dopant peak from 85 to 80 nm.

1.4.9 Time-resolved Fluorescence

1.4.9.1 Kinetics of the Blue Emission Band

Fluorescence lifetimes of different decay processes were investigated using the TCSPC technique. The charge carrier dynamics in doped and undoped ZnSe NCs was monitored following photoexcitation at 395 nm. Owing to the small Stokes shift (15-20 nm), the samples had to be excited with energy at least 15-20 nm higher than needed for the first excitonic transition to eliminate laser scatter in the decay trace. This excitation energy was low enough to ensure that the first or lowest energy exciton was created and hot electron relaxation dynamics would be minimized. The
samples did not show any sign of photo-bleaching during the course of measurements, which could otherwise introduce complications to the measurements.
The results, normalized by maximum amplitude, for time resolved emission between 430-460 nm are shown in Figure 1.11, with time scales varying from the 50 ns range in Figure 1.11 (a) and (b) to the 380 ns in Figure 1.11 (c). For the decay trace recorded at 430 nm on the short time scale (50 ns), where most of the PL comprises excitonic emission or emission from ST states, the undoped sample exhibits slightly larger amplitude of fast decaying components than that of the doped sample. At longer wavelengths, the amplitude of the slower-decay becomes more prominent for the doped sample. It is quite evident from the decay traces that overall fluorescence lifetime increases noticeably as the wavelength is changed from 430 to 460 nm.

The individual wavelength decay traces were fit using multi-exponential fitting with the rise being fit by the instrument response function (IRF) as collected from a scattering sample. Each decay trace, which was both wavelength and delay window dependent, was fit first with both lifetime and initial intensity as variable fitting parameters. The individual lifetime components were averaged and each decay refit with life time fixed and initial intensity as the variable parameter. This process was then reversed and the traces were fit with initial intensity fixed and lifetime as the variable fitting parameter. The individual lifetime components were re-averaged and the individual traces were again fit with initial intensity as the variable fitting parameter. As a result, one equation, \( f(t) \), was established which could describe the decay trace for any time window and any wavelength with initial...
intensity \((A_1, A_2, \ldots)\) being the only variable parameter, with \(y\) accounting for baseline correction; reported as Equation 1.1

\[
f(t) = y + \sum A e^{-t/\tau}
\]  

(1.1)

The time constants did not show any wavelength dependence over the observed wavelengths. On the time scale of 50 ns, the time-resolved PL decay profiles for both doped and undoped samples could be fit using the same multi exponential decay, yielding \(1.1 \pm 0.05\) \((\tau_1)\) and \(12 \pm 1\) ns \((\tau_2)\) time constants corresponding to the undoped sample and \(1.0 \pm 0.05\) and \(10 \pm 1\) ns for the doped sample (table 1.1).

**Table 1.1**: Lifetimes for various decay components in ZnSe:Cu and ZnSe NCs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\tau_1) (ns)</th>
<th>(\tau_2) (ns)</th>
<th>(\tau_3) (ns)</th>
<th>(\tau_4) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe:Cu</td>
<td>(1.0 \pm 0.05)</td>
<td>(10 \pm 1)</td>
<td>(100 \pm 10)</td>
<td>(630 \pm 130)</td>
</tr>
<tr>
<td>ZnSe</td>
<td>(1.1 \pm 0.05)</td>
<td>(12 \pm 1)</td>
<td>(60 \pm 10)</td>
<td></td>
</tr>
</tbody>
</table>

Fitting the data taken on the longer time scale of 380 ns generates one more decay component with the lifetime varying from \(60 \pm 10\) ns \((\tau_3)\) in undoped sample to \(100 \pm 10\) ns in the doped sample. The residual plots corresponding to the fitting of different decay
traces have been reported in Figure 1.12. Emission collected between 430-460 nm derives mostly from the recombination of trap-state electrons. These electrons must decay through phonons and wait for a compatible nuclear configuration before they can recombine with hole. A perfect fitting in this region generates a fast component decaying
within a few tens of ps which is ignored because it is on the same time scale as the instrumental resolution. The next fastest component with a lifetime of about 1 ns is attributed to the near band-edge emission or excitonic emission whereas the lifetime of 10 ns is assigned to emission from ST states which involve Zn dangling bonds. The slow decaying component (60 ns in undoped sample and 100 ns for the doped sample), probably corresponds to emission from DT states created by Se\textsuperscript{2-} dangling bonds or zinc vacancies, or self-activated emission involving a DAP recombination, as reported previously for Mn\textsuperscript{2+} doped sample[49].

Comparison of the time resolved decay curves for the doped and undoped samples can provide insight about the origin of emission bands in the blue region along with the effect of doping on various decay components. As the electrons residing in CB or ST states are delocalized, there would be a significant overlap between the electron and hole wave functions which results in faster decay due to higher exciton recombination probability. In addition, interstitial and surface defect states could be partaken by these delocalized electrons that further increase the decay rate for this emission. Both these factors justify that why emission decay at 430 nm has a larger amplitude fast component than that observed for 460 nm emission, as shown in Figure 1.11. Similar to the reports in other systems like CdS and ZnS,[23, 87, 88] a definite correspondence has been observed between the emission wavelength and the decaying rate where the emission decay is faster when it is closer to the bandedge. This is due to the reason that electrons/holes in the CB/VB or in ST
states are more delocalized as compared to the charge carriers in DT states, which results in more overlap of electron and hole wave functions leading to the faster decay.

The change in lifetime for DT state emission from 60 ns to 100 ns after doping is indicative of significant interaction between the dopant levels and DT states. This could be due to the reason that Cu\(^+\) being relatively negatively charged with respect to the neighboring lattice, acts as an efficient hole trap center so that the hole trap states of the host lying closer to the VB like the Cu\(^+\) state (Figure 1.8), can no longer trap the hole as effectively as in the case of undoped sample. This would result in DT state emission originating mostly from the hole trap states which are relatively deeper as compared to those involved in the case of undoped sample. With the hole trap states lying deeper in the doped system, there would be less overlap between the hole and electron wave functions due to the localization of deeper states which results in increasing the lifetime of DT state emission. A slight decrease in the lifetimes of short-lived components after doping suggests that the Cu dopant has some influence on the ST states as well. One possible mechanism is that the Cu dopant competes with the ST states in trapping the charge carriers from the CB or near bandedge states. Alternatively, lifetime shortening could be due to the increased density of trap states caused by the Cu dopant in ZnSe host.

1.4.9.2 Kinetics of the Green Emission Band

Emission from DT states constitutes the PL in the region from (~460-630 nm) for the undoped sample; whereas for the doped sample Cu related emission dominates in this region. Copper green emission, having maxima around 515 nm, has
significant overlap from trap state emission as indicated by the PL spectrum of the undoped sample (Figure 1.7) where the long tail of the near bandedge emission extends up to 570 nm. Therefore,

![Figure 1.13](image)

**Figure 1.13** (a) Time resolved emission decays of doped sample collected at 470, 490, 510, 530 and 560 nm. (b) 500 nm emission intensity vs time for undoped (green) and doped (blue) samples.

the first half of the green emission band in the doped sample would have considerable contributions from ZnSe trap states in addition to the dopant emission. To characterize the effect of the decrease in the DT state emission on the decay profile,
decay traces were collected at different wavelengths across the green emission band ranging from 470 to 560 nm as shown in Figure 1.13 (a); however, data for the undoped sample was collected only up to 500 nm due to the low intensity at longer wavelengths.

Figure 1.13 (b) shows the fluorescence decay collected at 500 nm for the doped and undoped samples. It is evident that the decay was faster in the undoped sample and the long-lived component of doped sample was quite pronounced. The wavelength dependent decay traces are reported in Figure 1.13 (a) for the doped sample which show that the amplitude of long lived component becomes increasingly dominant at longer wavelengths. The residual plots corresponding to the fits are shown in Figure 1.14.
A multi-exponential fit to the decay profiles of the doped sample collected in this wavelength region yields a long lived component with a lifetime of 600±130 ns. This slow decay component, present only in the doped sample, must be due to copper related emission. As the host peak in the doped sample was not completely eliminated, there might be some particles that were left undoped that could affect the relative amplitude of the decay components due to Cu versus trap states. However, this should not alter the kinetics of dopant or trap state emission.

Figure 1.14: Residual plots corresponding to the fitting of decay traces shown in Figure 1.13.
The percent contribution by each lifetime component to the overall fluorescence process was calculated for each decay profile of the series of wavelengths observed (Figure 1.15). To calculate percent contribution each wavelength dependent fitting function, which had only the initial intensity as the variable and was the sum of all individual lifetime components $f(t)$ (Equation 1.1), was integrated and compared to the integrated intensity for each individual component, an example of which is reported in Equation 1.2. This was taken to be the percent contribution from that lifetime component at a specific wavelength.

$$\text{% Intensity } (\lambda) = \frac{\int A_1 e^{-\frac{t}{\tau}} dt}{\int f(t) dt} \times 100$$

\hspace{1cm} (1.2)
Fitting the data in Figure 1.15, the intensity was calculated over the entire PL spectral range for each lifetime component. Subsequently, this data was used to deconvolve the PL spectrum as shown in Figure 1.16. This plot clearly indicates that the majority of the emitted photons coming from the doped sample are due to the Cu impurity. There is still a large portion of the photons coming from DT state emission, however it is interesting to note that this component has a maxima at relatively longer wavelength (500 nm) as compared to that of undoped sample (478 nm). This observation further supports the argument for increase in lifetime of DT states after doping.

As mentioned earlier, in the case of Cu green emission excitation of a VB electron to the CB is followed by the formation of a transient Cu$^{2+}$ acceptor. The subsequent capture of the electron by this acceptor is expected to be slow due to the low electron capture cross section of Cu$^{2+}$ [89]. At room temperature, the lifetime for Cu dopant in ZnS has been reported to be 500 ns[67] whereas in this study it is longer (630 ns) but nevertheless very close. The difference in lifetimes observed for ZnSe:Cu and ZnS:Cu may be partly due to different energetics of ZnSe as compared
to ZnS including bandgap location and bandgap energy but could also be due to variability in the non-radiative recombination pathways. Also, in the same work by Bol et al., the Cu lifetime at 4 K was reported to be 20 µs. As the quantum yield was measured to be 2-3% in this study, the radiative component was calculated to be $25 \pm 5$ µs, which is in agreement with the low temperature studies. The long lived radiative component is very similar to that of the triplet state emission observed in Cu$^+$ doped glasses at room temperature which was measured to be 41 µs.[90] It is, therefore, likely that the dopant emission in these systems involves a triplet as well; however, direct evidence of this has not been reported.

At longer wavelengths, it was expected that the major decay process contributing to emission would be coming from energy exchange to the Cu phosphor. This is also clear from the trend that relative ratio of amplitudes of fast components to that of slow components decreases as the emission wavelength is moved from left hand side of the dopant peak to the right hand side; **Figure 1.14(a).** However, this decrease in amplitude ratio which is due to decreasing overlap of trap state emission with dopant emission (**Figure 1.7**), does not affect the time constant for slow decay component due to copper.

### 1.5 Conclusions

Stable Cu-doped ZnSe NCs were prepared using octadecylamine as a capping agent. Adding the dopant at a stage where host NCs have developed well defined crystal facets, helped to adsorb copper strongly on to the NCs that would not be expelled on to the surface when ZnSe shell is grown. After solvent extractions to
remove the unreacted precursors, NCs stored in a mixture of hexanes and ODE are very stable and demonstrate quantum yield up to 3-8% even after months. Cu doping introduces efficient hole traps that quench emission involving hole trap states lying closer to the VB and significantly increases the lifetime of DT states probably due to decreased coupling in electron and hole trap states comprising DT state emission. In addition, Cu doping slightly decreases the lifetimes of fast decay components arising from excitonic and ST state emissions by competing with these states in trapping the charge carriers. The EXAFS results indicate that in the NC samples used for the EXAFS studies, many of the Cu neighbors are O atoms. This might arise from Cu mainly on or close to the NC surface. It is interesting that Cu appears to have four neighbors in ZnSe, and the Cu-Se bond length is close to the expected value, because for ZnS:Cu at low concentrations the number of S neighbors is closer to 3 and the Cu-S bond is compressed. The doping approach adopted is successful in preparing stable Cu doped semiconductor NCs, and time-resolved PL studies of the charge carrier dynamics is helpful in understanding their fundamental optical and electronic properties in relation to their structural characteristics revealed by EXAFS and other techniques.

1.6 References


CHAPTER 2: Effect of Al$^{3+}$ Co-doping on the Dopant Local Structure, Optical Properties, and Exciton Dynamics in Cu$^+$-doped ZnSe Nanocrystals

2.1 Abstract

The dopant local structure and optical properties of Cu-doped ZnSe (ZnSe:Cu) and Cu and Al co-doped ZnSe (ZnSe:Cu,Al) nanocrystals (NCs) were studied with an emphasis on understanding the impact of introducing Al as a co-dopant. Quantum confined NCs with zinc blende crystal structure and particle size of 6±0.6 nm, were synthesized using a wet chemical route. The local structure of the Cu dopant studied by extended X-ray absorption fine structure (EXAFS) indicated that Cu in ZnSe:Cu NCs occupies a site that is neither substitutional nor interstitial and is adjacent to a Se vacancy. Additionally, we estimated that approximately 25±8% of Cu was located on the surface of the NC. Al$^{3+}$ co-doping aids in Cu doping by accounting for the charge imbalance originated by Cu$^+$ doping and consequently reduces surface Cu doping. The Cu ions remain distorted from the center of the tetrahedron to one of the triangular faces. The lifetime of the dopant related PL was found to increase from 550±60 to 700±60 ns after Al co-doping. DFT calculations have been used to obtain the density of states of a model system to help explain the optical properties and dynamics processes observed. This study demonstrates that co-doping using different cations with complementary oxidation states is an effective method to enhance optical properties of doped semiconductor NCs of interest for various photonics applications.
2.2 Introduction

Colloidal semiconductor NCs or quantum dots (QDs) have been studied extensively due to their potential applications in economical, solution processable devices. The intriguing optical and electronic properties of the NCs, originating from quantum confinement effects and large surface-to-volume ratio,[1-7] make them emerging candidates for applications in solid-state lightening,[8, 9] biomedical labeling,[10-12] photovoltaics,[13, 14] lasers,[1] and electronics.[15] Their properties can be varied in a controllable manner by changing the size, shape, surface functionalization, and/or by introducing small quantities of dopant atoms. Doped semiconductor NCs constitute an important subclass of nanomaterials where a small amount of impurities is intentionally incorporated into the host material, thus adding another degree of freedom for altering their optical, electronic, and magnetic properties.[16-20] Doped nanomaterials possess unique properties which are important for imminent applications, including: longer excited state lifetimes, minimum self-absorption, broad emission spectral window, and thermal stability.[21-24]

Copper doped II-VI semiconductor NCs have been the subject of great interest in recent years due to their potential as bright visible light phosphors with size-tunable emission.[22, 25, 26] The low toxicity and large Stokes shift of Cu-doped ZnSe NCs makes them an attractive candidate for lighting and display applications.[27, 28] However, the synthesis of Cu-doped ZnSe can be quite challenging because there is a large difference in the solubilities of copper selenide
and zinc selenide (with $K_{sp}$ values of $10^{-57.7}$ and $3.6 \times 10^{-26}$, respectively)[29, 30] which renders their co-precipitation rather difficult. As observed in our recent study, copper enters ZnSe as $\text{Cu}^+$ and mostly stays on or closer to the surface of the host.[31] The $+1$ oxidation state would require the copper ion to accompany defect structures, specifically selenium vacancies ($V_{\text{Se}}$), for charge compensation. A possible route to stabilize Cu in the host lattice could be co-doping with a group III element, which accounts for the charge imbalance and acts as a coactivator as well. Coactivators have been found to introduce donor levels just below to conduction band (CB)[32] and enhance the donor-acceptor pair (DAP) emission, which is the primary emission seen in these systems.[33]

To better implement the approaches for rational design of these doped semiconductor NCs, it is critical to improve the understanding of optical properties of this class of NCs, which depend strongly upon the local structure around the luminescence centers. The local structure around the dopant ions is influenced by the oxidation state mismatch and ionic size difference between the dopant and the host cation. Photogenerated electrons and holes are expected to decay through these impurity ion luminescence centers with different transition probability and decay rates as compared to the host. Especially for NCs, the optical properties and dynamical processes will be sensitive to the local structure of the dopant atoms due to a strong interaction between the quantum confined exciton and the dopant site. Therefore, it is extremely important to obtain a clear, atomic level picture, of the local structure surrounding the Cu ion in these systems, including: the location of dopant
ion in the NCs, local distortions in bond distances, and oxidation state of the dopant. Since the concentration of Cu is relatively low in these materials (0.5% of the total Zn content) and because it is difficult to differentiate between Zn and Cu by standard X-ray diffraction (XRD); EXAFS as an element specific technique which is sensitive only to the first few neighboring shells, emerges as one of the most powerful techniques to resolve the local structure around the Cu atoms. Although some studies have been done on Cu-doped ZnS NCs,[34, 35] such detailed investigation of Cu doped ZnSe system is lacking.

In conjunction with the structural properties’ studies, the investigation of optical properties of the ZnSe:Cu and ZnSe:Cu,Al systems using steady state and time resolved photoluminescence techniques can help to gain insight into the correlation between the structural and optical properties as well as the associated electronic energy levels. In addition, dynamics studies of the exciton or charge carriers can provide useful information about the various photophysical processes involved. For example, it has been reported previously that the inclusion of Cu in ZnSe can extend the fluorescence lifetime from 10 to 600 ns.[31] This effect was attributed to the transient formation of Cu$^{+2}$ after the hole becomes trapped by Cu$^+$ forming a stable hole state within the NCs. These studies are aimed at optimizing the photoluminescence properties for potential functional applications of the doped semiconductor NCs.

In the present work, we have synthesized and determined the local structure of the dopant ion in ZnSe:Cu and ZnSe:Cu,Al NCs using EXAFS. Their optical
properties have also been characterized with emphasis on photoluminescence. In addition, the exciton and charge carrier dynamics of these NCs have been investigated using time-correlated single-photon counting (TCSPC) combined with integrated singular value decomposition (SVD) global fitting to elucidate the wavelength dependence of the fluorescence recombination pathways thereby allowing for a regimented correlation between their structural and optical/dynamic properties. Furthermore, density functional theory (DFT) calculations aimed at understanding the electronic structure of the Cu related states have been performed using structural information obtained by EXAFS to gain a precise picture about the active energy levels involved during electronic transitions. EXAFS studies indicated that Cu impurity occupies a site that is neither an interstitial site nor a high symmetry substitutional. Most importantly, co-doping with Al eliminated anion vacancies around the Cu site and improved the PL yield by increasing the lifetime of Cu related emission.

2.3 Experimental section

2.3.1 Materials

Zinc stearate (technical grade), octadecene (ODE, 90%), tributylphosphine (TBP 97%, mixture of isomers), copper acetate (98%), octadecylamine (ODA, 99%), copper acetate (99.9%) and chloroform (anhydrous) were from Sigma-Aldrich. Se powder (<325 mesh, 99.7%) was purchased from Acros Organics, and anhydrous zinc acetate (99.98%) along with cuprous selenide (99.999%), cupric selenide (99.999%) and boron nitride (99.5%) were bought from Alfa Aesar. Methanol (99.9%) and
Acetone (99.7%) were purchased from Fisher Scientific. All the chemicals were used without further purification.

2.3.2 Synthesis of Doped ZnSe NCs

Doped ZnSe NCs were synthesized following the method of Peng et al.,[22] with some modification as reported previously.[31] Briefly, 0.12 g zinc stearate in 20 ml ODE was heated up to 300 °C in a 50 ml three-neck flask under argon flow. To this solution of ZnSt₂, was injected a 3 ml degassed mixture of Se powder (0.080 g) dissolved in 0.80 g TBP along with 0.30 g ODA and diluted with ODE (2 ml). The heat was removed 30 seconds after the injection and the mixture was cooled to 200 °C at which point the sample was equally divided between two flasks; one part for making the Cu doped sample and the second one for the Al co-doped sample. The purpose of using the ZnSe cores from the same batch for both doped and co-doped NCs is to minimize the subtle differences between the samples. For ZnSe:Cu, a calculated amount of copper (Cu being 0.5% of total Zn content) stock solution (1.074 x 10⁻³ g copper acetate dissolved in 1.25 g TBP) was added drop-wise to ZnSe cores at 200 °C. The temperature was then slowly ramped up to 240 °C and maintained for two hours during which 0.15 ml aliquots of zinc acetate solution (0.1M solution in TBP diluted to 0.05M with ODE) as well as selenium solution (as mentioned earlier), were added at regular intervals until no change was observed in the PL spectra. A pure ZnSe sample was synthesized similarly without adding any impurities and Al co-doped sample was prepared the same way except that calculated amount of aluminum stearate suspension (in ODE) was added along with copper
acetate solution. To monitor the absorption and PL spectra, small aliquots (~0.2 ml) were taken from the flask with a syringe and diluted to an optical density between 0.2 and 0.3 at 390 nm using chloroform. The unreacted precursors were solvent extracted twice from the crude sample by mixing it with a mixture of chloroform and methanol (1:4). To isolate the solid particles, NCs in ODE phase were precipitated using acetone, recovered by centrifuging, and stored under argon.

2.3.3 Structural and Spectroscopic Measurements

A Hewlett Packard 8452A diode array spectrometer was used to measure the UV-Visible spectra at room temperature. PL spectra were recorded using a Perkin-Elmer Luminescence spectrometer. PL QY of NCs was calculated by comparing the integrated PL intensity of the NCs (PL_{NC}) in chloroform to that of perylene dye in ethanol.\cite{36} The absorption of the dye (Abs_{dye}) and each NC sample (Abs_{NC}) at the excitation wavelength (390 nm), the temperature, and the refractive indices of the solvents were taken into account for QY calculation using Equation 2.1.

$$QY = QY_{dye}^{PL_{NC}} \frac{Abs_{dye}^{n_{chloroform}}}{Abs_{NC}^{n_{ethanol}}}$$  \hspace{1cm} (2.1)

Low-resolution TEM measurements were performed on a JEOL model JEM-1200EX microscope at 80 KV. High-resolution TEM (HRTEM) images were obtained at Lawrence Berkeley National Laboratory using a Philips CM300-FEG at the National Center for Electron Microscopy.

Elemental analysis was performed with inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin-Elmer Optima 4300DV. To
remove the excess precursors, NCs were repeatedly purified using Sorvall RC-5C Plus centrifuge that was used at 14000 rpm at room temperature to crash the NCs, and then dried before digesting them in Optima-grade HNO₃:HCl mixture (aqua regia). The digested samples were diluted with milliQ water and pumped at a rate of 1.5 ml/min into the plasma chamber.

Rigaku Americas Miniflex Plus powder diffractometer was used for XRD measurements utilizing Cu Kα (λ = 1.5405 Å) as the incident radiation. Diffraction patterns were recorded at a rate of 2° per minute with a step size of 0.04°.

Zn and Cu K-edge X-ray absorption near edge structure (XANES) and EXAFS data were collected at the Stanford Synchrotron Radiation Light source (SSRL), on beamline 7-3 at 10 K with an average current of 300 mA and at electron energy of 3.0 GeV. The radiation was monochromatized using a Si (220) double crystal monochromator, which was detuned to 50% of its maximum at the Zn/Cu K-edge to minimize the effects of higher harmonics. The beam size on the sample was reduced to 0.5 mm vertical and 1.0 mm horizontal FWHM, and intensity of the incident x-rays (I₀) was monitored by a N₂ filled ion chamber in front of the sample. Zn data was collected in transmission mode whereas, due to low concentration, Cu data were collected in fluorescence mode using a 30 element Ge detector (Canberra), with the samples at 45° to the incident beam. The energy was calibrated by using the rising edge positions of Cu foil (8980.3 eV) and Zn foil (9660.7 eV). Cu K-edge data was collected for NC samples along with that of Cu₂Se and CuSe standards. For the EXAFS studies, samples were deposited on plexiglass sample holders with kapton
film windows. In the case of Cu$_2$Se and CuSe standards, the samples were diluted with boron nitride to a concentration of 0.3%, and sandwiched between two layers of Mylar tape.

Standard programs\[37\] based on IFEFFIT library,\[38\] were used for data reduction and fitting. While reducing fluorescence data, the pre-edge background was fit to a line with a constant baseline whereas the post-edge background was fitted to a spline function. In the case of transmission data, the pre-edge and post-edge backgrounds were fit to a Victoreen and spline function, respectively. The extracted $k$-space data, $k^3 \chi(k)$, averaged over 5 scans, was then used to FT the data into r-space. For Zn K-edge, a $k$-space window of 3.5-14.0 Å$^{-1}$ was used for FT, whereas for Cu K-edge data the FT range used was 3.5-11.0 Å$^{-1}$. The window function used consisted of a rectangular part in the center and Hanning parts on the sides having a Hanning fraction\[39\] of 0.2.

Time resolved PL studies of the ZnSe:Cu and ZnSe:Cu,Al samples were performed at room temperature using TCSPC as described in our previous report.\[31\] Briefly, a Ti:sapphire crystal (Kapteyn-Murnane Laboratories, Model: MTS Mini Ti:Saphire) was pumped with a 5W Coherent Verdi-V5 (532 nm) laser to produce a tunable, mode-locked laser line between 790-820 nm with a frequency of 100 MHz. A pulse picker (Conoptics, model 350-160) was utilized to prepare a pulse train of 0.5 MHz, after which the 790 nm light was frequency doubled to 395 nm using a BiBO crystal. After separating the 790 and 395 nm light with a dichroic mirror, the 395 nm (50 ps pulse width) was then used to excite the NCs sample in chloroform. The PL
was collected at 90° with respect to the incident laser and passed through a magic angle polarizer followed by a monochromator with a resolution of 0.25 nm. The monochromatic light was then focused on an avalanche photodiode where photons were counted in a reverse stop-start mode.[40]

A number of time windows were collected to investigate the wide range of time constants observed in the decay spectrum of these samples, and were 50, 380, and 2000 ns for individual emission wavelengths ranging from 450 to 650 nm. The NCs were probed using a 50 ns window over 4096 channels, 380 and 1000 ns windows over 1024 channels and a 2000 ns window over 256 channels. The instrumental resolutions were 0.05, 0.32 and 0.70 ns for 50, 380 and 2000 ns time windows, respectively. Data was analyzed using an IGOR Pro-based (wavemetrics) macro procedure developed in-house.

2.4 Results and Discussion

2.4.1 UV-Visible Absorption and PL

The UV-Visible absorption spectra of both the ZnSe:Cu and ZnSe:Cu,Al samples are shown in Figure 2.1(a). The spectra show an absorption onset around 422 nm and first exciton peak around 403 nm which is due to the band edge excitation of the host and exhibits quantum confinement effects. There is not any noticeable difference between the absorption spectra of the two samples, indicating that Al co-doping has essentially no effect on the electronic absorption spectrum of ZnSe, which is not unusual.
The PL spectra shown in Figure 2.1(b) exhibit a broad emission peak (FWHM ~ 80 nm) centered at 540 nm and 530 nm for the ZnSe:Cu and ZnSe:Cu,Al, respectively. The samples show minimal host related emission at 430 nm indicating the complete Cu doping in both cases. There is no considerable difference in the spectral features between the two samples with similar optical density (0.2 O.D.) at the excitation wavelength of 390 nm. It is evident that samples differ in PL QY: about 3% for ZnSe:Cu NCs and 7% after co-doping with Al. The lower QY in
ZnSe:Cu is likely due to electron trap states associated with V_{Se} defects which originate from the charge compensation required as a result of the Cu^{+}-doping. Introducing Al^{3+} would account for the charge imbalance resulting in the removal these trap states and thereby, decreasing the trap-mediated non-radiative electron-hole recombination. The PL emission in Cu-doped ZnSe has been attributed to the electronic transition from the CB or a shallow donor level, optionally introduced by the co-dopant or unintentionally by oxygen,[41] to the Cu d-states.[42] The PL arises from the initial photoexcitation of a valence band (VB) electron to the CB in the host ZnSe. The CB electron then might get trapped by shallow trap (ST) states, surface dangling bond (DB) states, or impurity donors such as Al or oxygen. The hole generated in the VB then moves to Cu^{+}, creating a transient Cu^{2+} acceptor state. Depending upon the ligand geometry surrounding the Cu, the d-states of Cu^{2+} are split by the ligand field, resulting in multiple possible hole acceptor states which has been previously regarded as the reason for the broad Cu related emission band; with a FWHM of ~80 nm.

2.4.2 Crystal Structure, Size and Composition

Powder XRD patterns for both samples are shown in Figure 2.2.(a) which represent zinc blende ZnSe structure, according to the data in the Joint Committee on Powder Diffraction Standards (JCPDS) Card (File No 80-0021). Peaks corresponding to the (111), (220), and (311) lattice planes are indexed. No change in the crystalline phase is observed by co-doping with Al. Using Debye-Scherrer formula, the crystallite size of NCs was calculated to be ~6 nm from the line width of (111) peak.
A representative TEM image of the NCs is presented in Figure 2.2(b) along with the histogram and a HRTEM image as the insets. The diameters of 100 particles were measured using the ImageJ program[43] (distributed by NIH) to obtain the histogram. The average particle size was obtained to be 6 nm with a size distribution of 10%, as shown in the inset of Figure 2.2(b). It is clear from the HRTEM images and from XRD that Cu did not precipitate as a separate phase like copper selenide as a separate particle or on the surface or the ZnSe NCs.
The relative concentrations of Zn, Se, Cu, and Al were measured using inductively coupled plasma optical emission spectrometry (ICP-OES), the results of which are presented in Table 2.1. The Zn:Se ratio and relative Cu percent was essentially the same between the ZnSe:Cu and ZnSe:Cu,Al samples. Additionally, the results confirm the presence of Al in the co-doped system at a similar mole ratio as the Cu indicating that Cu and Al dope into ZnSe as 1:1. This result confirms our previous assertion that Cu dopes ZnSe as a monovalent cation requiring charge balance by the trivalent Al cation.

Figure 2.2: (a) XRD pattern of ZnSe:Cu (red) and ZnSe:Cu,Al (green) samples exhibiting zinc blende crystal structure. (b) TEM image of NCs with inset showing HRTEM image of a single nanocrystal along with the histogram.
Table 2.1: ICP-OES analysis of ZnSe:Cu and ZnSe:Cu,Al NCs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar Zn/Se ratio</th>
<th>% of Cu of total</th>
<th>% of Al of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe:Cu</td>
<td>1.09</td>
<td>0.49</td>
<td>----</td>
</tr>
<tr>
<td>ZnSe:Cu,Al</td>
<td>1.13</td>
<td>0.52</td>
<td>0.60</td>
</tr>
</tbody>
</table>

2.4.3 Cu K-edge XANES

The XANES spectra of the two samples are presented in Figure 2.3(a) along with the standard samples including Cu foil and Cu$_2$Se. XANES is sensitive to the nature of chemical bonding, oxidation state, and local structure around the atom being probed. The fine structure of the spectrum for ZnSe:Cu,Al differs considerably from

![Figure 2.3](image_url)

**Figure 2.3:** (a) A comparison of Cu K-edge XANES for ZnSe:Cu, ZnSe:Cu,Al, Cu$_2$Se and Cu metal. The plots were normalized at higher energies. (b) Magnitude of the Fourier transform of experimental EXAFS functions $(k^3 \chi)$ in ZnSe:Cu, ZnSe:Cu,Al and Cu$_2$Se for Cu K-edge along with that of Zn K-edge of ZnSe NCs.
that of the ZnSe:Cu in the energy range 8986-8997 eV, indicating that Al is incorporated in the vicinity of Cu ion. The fine structure of the Cu$_2$Se is quite different from both of the Cu doped NC samples. However, the edge position is consistent with +1 oxidation state of Cu.[44] Also, in the case of $K$-edges of transition metals with partially filled $d$-states, a pre-edge peak is observed due to transition from $1s \rightarrow 3d$ states. Such transitions are dipole forbidden, but become weakly allowed due to hybridization with $p$ states. In the case of Cu $K$-edge, a pre-edge would be expected if the ion were in a +2 oxidation state (3$d^9$ electronic configuration) as reported in the case of Cu ions with empty $d$-states.[45, 46] The absence of such a pre-edge peak in our data (Figure 2.3a) is further evidence of Cu being in +1 oxidation state in these NCs.

2.4.4 EXAFS

The Fourier transform (FT) of the Cu $K$-edge EXAFS data for the ZnSe:Cu and ZnSe:Cu,Al samples are shown in Figure 2.3(b) along with the Zn EXAFS from the ZnSe NCs as well as the Cu EXAFS from the Cu$_2$Se standard, for comparison. The EXAFS data at Zn $K$-edge of the ZnSe:Cu NCs confirms that the Cu local structure in ZnSe:Cu is different from that of Zn and that the Cu doping is not a simple substitution of Zn. In Figure 2.3(b), the x-axis is the apparent distance, that is approximately 0.5Å shorter than the actual distance due to the phase shift.[47] The first peak in these traces corresponds to the nearest neighbor Se atoms in cubic ZnSe. It is clear that first peak positions for Cu are slightly shorter than that for Zn. Since Cu and Zn are neighboring elements in the periodic table and the backscattering atom
is Se in all the cases here, the profound differences among the traces are due to different local structures around the absorbing atoms. In addition, the Cu EXAFS for the ZnSe:Cu and ZnSe:Cu,Al samples differ from each other; the peak in the former is asymmetric, appears at slightly shorter distance, and has lower amplitude as compared to the more symmetric peak of ZnSe:Cu,Al. The asymmetry and comparatively reduced amplitude in ZnSe:Cu indicate that there is more than one type of Cu centers. Although the amplitudes are quite different, the first shell peak position for Cu$_2$Se aligns well with that of ZnSe:Cu,Al. This implies that Cu$^+$ ions in these two might occupy sites of similar symmetry.

2.4.5 Zn EXAFS

FEFF8 was used to construct the theoretical EXAFS paths from the ZnSe zinc blende structure which was used as the starting model.[48] For fitting the Zn K-edge data of ZnSe NCs, three single scattering (SS) paths were used which include Zn-Se (2.45 Å), Zn-Zn (4.00 Å) and a longer Zn-Se (4.70 Å), with the bond lengths being constrained to the cubic ZnSe structure (only allowing small variations). The amplitude reduction factor ($S_0^2$), which accounts for the many body effects such as shake up/off process at the absorbing atom, was obtained from the bulk ZnSe and fixed to 0.81. The coordination number (N) of the first shell was fixed to N=4 while the N number of the second and third shell was allowed to vary since a considerable number of the NC atoms are on the surface which may lead to a reduced average number of second and third shell neighbors from N=12 in the bulk. The fit obtained is shown in Figure 2.4 (a) that agrees well with the experimental data. The values for
the Debye-Waller factor ($\sigma^2$) were 0.004, 0.006, and 0.008 Å$^2$ for the three SS paths used. The complete results of the fit are reported in Table 2.2 of the supporting information and agree well with experimentally determined parameters of bulk ZnSe,

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**Figure 2.4:** (a) R-space data (blue) for ZnSeNCs at the Zn K-edge along with the fit (red) carried over the r-space ranging 1.1-4.7 Å. The fast oscillation represents real part of FT. The data were fit to a sum of three peaks: Zn-Se, Zn-Zn and a longer Zn-Se (for the fit parameters see Suppl Table S1, ZnSe NCs). (b) Fit # 2 (red) of the Cu EXAFS data (green) for ZnSe:Cu sample carried over the range of 1.3-2.7 Å (See suppl Table S1, ZnSe:Cu Fit#2). A Cu-O shell had to be included to account for the surface Cu content which turned out to 25±8% of the total Cu. (c) Structural model for local structure around core Cu showing two neighboring Cu ions accompanying a Se vacancy. Atom colors are: Zn (purple), Se (yellow), and Cu (pink). (d) R-space data (green) for ZnSe:Cu,Al sample including the fit # 2 (red) to the first shell, carried out over the range of 1.3-2.7 Å. For this fit Cu-Se distances for three Se first neighbors were restrained around 2.34 Å, whereas the distance was allowed to vary for the fourth Se.
except that the number of second and third neighbors was found to be 9.1±0.4 and 7.6±0.4, respectively, which is less than that of bulk ZnSe (N=12).[49, 50]

### 2.4.6 Cu EXAFS

Since Cu\(^+\) replaces a Zn\(^{2+}\) cation in the ZnSe lattice, a number of charge compensated models have been proposed to correct the charge imbalance caused by Cu doping. The two primary models are: i) two Cu\(^+\) ions replace two Zn\(^{2+}\) ions and an accompanying neighboring Se\(^{2-}\) vacancy (V\(_{\text{Se}^{2-}}\)) is created,[51] and ii) one Cu\(^+\) substitutes for one Zn\(^{2+}\) ion (Cu\(^+\)\(_{\text{Zn}}\)) and a second dopes at an interstitial site, Cu\(_{\text{i}}^+\).[52, 53]

Initially, theoretical EXAFS functions were calculated using FEFF8 starting from the known cubic ZnSe structure and replacing the central Zn atom with Cu. The S\(_0^2\) parameter was determined empirically by fitting the Cu EXAFS data for CuSe (data not shown here), and was fixed to 0.83. Using these Cu-Se parameters from the ZnSe:Cu\(_{\text{Zn}}^+\) model, no reasonable fit could be obtained as expected. One such fit is shown in Figure 2.5 and Table 2.2 (ZnSe:Cu Fit # 1) in which the Cu-Se bond distances were allowed to vary during the fit procedure, as we expect Cu-Se to be shorter than Zn-Se distance. As mentioned, the FT first peak is asymmetric indicating the contribution from more than one type of Cu centers, likely from Cu atoms on the surface of the NC. Consequently, we added a Cu-O path which represents the surface Cu coordinated to octadecylamine (ODA), water, or oxygen (in the case Cu gets oxidized). Also, the first neighbor peak (Cu-Se) is expected to be at a similar or shorter bond distance compared to ZnSe, therefore, a variable parameter of Cu-Se
bond distance was used during the fit. A good fit was obtained as shown in Figure 2.4 (b) (Table 2.2 ZnSe:Cu Fit # 2). For this fit, the reduced chi-square value decreased by more than half of its value by including a Cu-O path ($\chi^2_{\text{red}}$ decreased from 289 to 47), which indicates the validity of the additional path. With this fit, the number of nearest Cu-Se neighbors was found to be 2.7±0.3 for the core Cu, while a shorter Cu-O fraction was about 0.9±0.3. This implies that a major fraction of interior Cu must be accompanying a Se vacancy, and the surface Cu site was estimated to be 25±8% of the total Cu content. A local structural model of internally doped Cu$_{\text{Zn}}^+$ is shown in Figure 2.4 (e) with two neighboring Cu ions along with the V$_{\text{Se}}$. The Cu-Se distance was found to be 2.34 Å which is 0.11 Å shorter than the bond distance if Cu were substitutional to Zn (Zn-Se is ~2.45 Å). A similar defect structure has been

Figure 2.5: Cu EXAFS data (blue) for ZnSe:Cu along with the fit # 1 (red) without taking into account the surface Cu site but allowing Cu-Se distance to vary.
reported recently for Cu-doped ZnS that shows that Cu accompanies a Se vacancy.[54]

It is interesting to note that there is no second neighbor peak in the ZnSe:Cu EXAFS. Even though a considerable amount of Cu is estimated to be on the surface, it is expected to have enough Cu-Zn second neighbors which would result in second neighbor

![Figure 2.6: Cu EXAFS data (blue) for ZnSe:Cu along with the fit # 3 (red) carried over a range of 1.1 to 4.4 Å.](image)

peak.[54] However, if Cu is displaced away from a V_{Se} and gets closer to the remaining three Se by 0.11 Å, which corresponds to an off-center displacement of Cu by~0.46 Å, the twelve Zn second neighbors would no longer be equidistant from the absorbing Cu. In this case, the Zn second neighbors would contain three groups: three of them being around ~3.6 Å from Cu, six with almost unchanged distance at ~4.0 Å, and the remaining three would be at a distance of ~4.4 Å. With such variability in the second neighbor distances, the second neighbor peak would split by approximately
$1/3 \, \text{Å}$ and the real parts of the FT would be out of phase for each component, resulting in small amplitude between 3-4 Å, as was seen in the r-space data. Using the parameters of this defect structure around Cu, a fit was carried out over the longer range of 1.1-4.4 Å and is shown in Figure 2.6 (Table 2.2 ZnSe:Cu Fit # 3). The fit agrees well with the data having a small amplitude between 3-4 Å.

Table 2.2: Local structure parameters for Zn and Cu in nanocrystal samples determined after fitting the Fourier transformed data. ZnSe bulk parameters are also shown. Debye-Waller factor ($\sigma^2$) was used as a variable parameter whereas $S_0^2$ value was fixed to 0.81 for Zn and 0.83 for Cu data.

<table>
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<th>Sample</th>
<th>Fit #</th>
<th>Path</th>
<th>R (Å)</th>
<th>N</th>
<th>$\sigma^2$ (Å²)</th>
<th>$\Delta E_0$ (eV)</th>
<th>R-factor</th>
<th>$\chi^2_{\text{red}}$</th>
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<td>Zn-Se</td>
<td>2.45</td>
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<td></td>
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Cu-Zn2
Cu-Zn3
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Cu-Zn2
Cu-Zn3
ZnSe:Cu,Al
Cu-Se
Cu-Se
Cu-Se
Cu-Se
Cu-Zn1
Cu-Zn2
Cu-Zn3

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<td>0.012</td>
<td>0.019</td>
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<td>-2.42±1.0</td>
<td>-3.92±2.0</td>
</tr>
<tr>
<td>%</td>
<td>190</td>
<td>99</td>
<td>52</td>
<td>0.091</td>
<td>0.002</td>
<td>0.002</td>
</tr>
</tbody>
</table>

For Zn EXAFS, a fit region of 1.1 ≤ R (Å) ≤ 4.7 was used. In the case of Cu EXAFS for ZnSe:Cu and ZnSe:Cu,Al, fit # 1 and 2 were carried over the r-range 1.3 ≤ R (Å) ≤ 2.7 for each sample, whereas data were fit in the range 1.1 ≤ R (Å) ≤ 4.4 for fit # 3 in both the samples. Regarding k-space, a range of 3.5 ≤ k (Å⁻¹) ≤ 14 was used for Zn EXAFS, whereas a k-space window of 3.5 ≤ k (Å⁻¹) ≤ 11 was used for Cu EXAFS data.

In the case of Cu⁺, there are two possible interstitial sites in the zinc blende structure as addressed by Goldman et al.[50] One of the interstitial sites has four Se nearest neighbors at 2.45 Å and six Zn neighbors at 2.83 Å, whereas the second site has four Zn nearest neighbors at 2.45 Å and six Se neighbors at 2.83 Å. FEFF8 was used to calculate the EXAFS functions for both Cu⁺ possibilities by starting with the cubic ZnSe and placing the central Cu at interstitial site. We carried out the fits by adding the Cu-Zn peak around 2.83 Å for Cu⁺ and restraining the Cu-Zn pair distance to ±0.05 Å around the nominal distance. In all such fits, with varying fractions of
Cu$_i^+$, the amplitude corresponding to the interstitial peak turns out negligible. Similar results were obtained for the second interstitial site with Zn first neighbors and Se second neighbors. Therefore, we concluded that the fraction of Cu$_i^+$, if present, is negligible.

For the ZnSe:Cu,Al sample, theoretical FEFF functions were generated from a model by starting with the cubic ZnSe structure, replacing one Zn with Cu and another Zn, in the nearest neighbor shell, by Al. No reasonable fit was obtained using these theoretical functions. The closest fit obtained for the first shell, when the Cu-Se distances were allowed to vary, is presented in Figure 2.7. The coordination number of Cu-Se corresponding to this fit was 3.6±0.3 and the R-factor value, which is a measure of the absolute misfit between the data and the fit, was 0.091 (Table 2.2, ZnSe:Cu,Al Fit # 1).

![Figure 2.7: EXAFS data (blue) at Cu K-edge for ZnSe:Cu,Al including the fit # 1 (red) when allowing the Cu-Se distance to vary.](image)
Another possibility could be considered based on the recent crystal structure studies of Cu$_2$Se by Gulay et al.[55] They reported that Se ions are in close-packed arrangement making layers in ABC sequence, with Cu ions occupying all the tetrahedral interstices. It was reported that, out of 12 Cu ions of the unit cell, 11 of them are shifted from the center of the tetrahedral site towards the edge or one of the faces of the tetrahedron. Not only the individual Cu-Se bond distances are different in this crystal structure, but also they are different from other Cu centers of the unit cell. Such anisotropic distribution of Cu could well explain the reduced amplitude of the first peak and the absence the second neighbor peak in the FT of Cu$_2$Se EXAFS (Figure 2.3b), which further supports the argument above for the negligible amplitude of the second neighbor peak in the NC sample. In addition, the amplitude of the peak for Cu in Cu$_2$Se is smaller than that in the NCs (Figure 2.3b). This might suggest that the Cu ions in the NCs have less anisotropy in their distribution and prefer a certain triangular plane of the tetrahedron, instead of a random distribution, as in Cu$_2$Se. This would further support the argument that Al occupies a site in the vicinity of Cu causing it to prefer a particular triangular facet of tetrahedron.

Keeping in view the crystal structure of Cu$_2$Se, we carried out another fit with two Cu-Se paths such that for the first path Cu-Se distance was restrained around 2.34 Å, whereas the distance was allowed to vary for the second one. The resulting fit (Fit # 2) for the first shell is shown in Figure 2.4 (d) and agrees very well with the data. For this fit, the Cu-Se distances are 2.35 Å, corresponding to a coordination number of 2.8±0.2, and a second Cu-Se distance of ~ 2.67 Å, corresponding to a coordination...
number of 0.9±0.2 (Table 2.2, ZnSe:Cu,Al Fit#2). This indicates that the Cu site is not exactly substitutional; not only does the Cu move closer to three Se, but the forth Se likely becomes displaced from its position and moves towards the Cu as well. Again the displacement of Cu from the center of tetrahedral site would split the Cu-Zn second neighbor peak into three: one at a distance shorter than normal, one at almost the nominal pair distance, and the third one at a longer distance. Such a splitting is expected to reduce the amplitude for the second neighbor peak as described earlier. This may be a reason that no substantial amplitude is observed between 3 and 4 Å in the r-space data as exhibited in the Figure 2.3(b). A fit carried over the longer range (1.1-4.4 Å) starting with the parameters corresponding to this distorted Cu site is shown in Figure 2.8 (Table 2.2, ZnSe:Cu,Al Fit#3).

To find out the fraction of surface Cu in ZnSe:Cu,Al sample, a Cu-O path was added in the EXAFS. However, the quality of fit did not improve considerably; the contribution was negligible and an increase in reduced chi-square was observed. Therefore, we conclude that there is little surface Cu in this sample, if any. Hence, Al$^{3+}$ not only compensates the charge imbalance, but also enhances the solubility of the Cu in the host resulting in internally doped NCs. As observed in the ZnSe:Cu, the inclusion of Cu$_{i}^{+}$ into the fitting model did not improve the fit.
Figure 2.8: EXAFS data (blue) at Cu K-edge for ZnSe:Cu,Al including the fit # 3 (red) carried over the range 1.1 to 4.4 Å.

2.4.7 DFT Calculation of Density of States

The electronic structure of the ZnSe NCs before and after Cu doping was studied using DFT with the PBE functional, ultra-soft pseudo potentials, and plane wave basis sets. The density of states (DOS) for the host material was calculated for a 64 atom supercell and is presented in Figure 2.9 (a). The Cu-doped ZnSe NC system was studied with a 63 atom supercell in which two Zn atoms were replaced for Cu and the Cu-Se nearest neighbor distance was distorted to the bond distance measured by EXAFS placing Cu in a distorted trigonal geometry. The forth Se, shared by both Cu dopants, was removed forming a \( V_{Se}^{-2} \). The Zn \( s \) and Se \( p \) DOS obtained from this calculation are shown in Figure 2.9 (a). The VB is due to Se \( p \).
Figure 2.9: (a) Partial DOS for Se p (red) and Zn s (purple) and Cu e (brown) and \( t_2 \) (green) states, calculated with the 63 atom super cell, as well as for the VSe state caused by Cu doping which are related to the Zn s dangling bond orbital (blue). (b) Partial DOS for Se p (red), Zn s (purple), Cu e (brown), Cu \( t_2 \) (green), Al s (light blue), and Al p (dark blue) states. The total density of states (DOS) of ZnSe 64 atom super cell (solid black) shown in both (a/b).

states while the CB is from strongly hybridized Se p and Zn s orbitals, as was also the case in the ZnSe system. The integrated local density of states (LDOS) can be seen in Figure 2.10. The Cu \( d(e) \) and \( d(t_2) \) DOS as well as the VSe\(^{-2} \) related states (which is the dangling bond Zn s orbital) are also shown. These states were multiplied by a scaling factor in order for them to be visible against the VB and CB states making the vertical axis arbitrary in Figure 2.9. The Cu \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals (collectively, \( d(e) \)) were found to be strongly hybridized with the VB Se p states and contribute to the VB edge. This result is contrary to the currently accepted model which places the \( e \) orbitals above the VB edge.[26] The Cu \( d_{xz}, d_{yz}, \) and \( d_{xy} \) \( (t_2) \) states are found to be above the VB edge within the bandgap \( (E_g) \). The five Cu \( d \) orbital DOS can be found in the Figure 2.11. Using a Gaussian peak to fit the Cu \( t_2 \) DOS peaks, the Cu \( t_2 \) states are \( E_{VB} + 0.31 \text{ eV} \) and have a FWHM of 120 meV. The state associated with VSe has
Figure 2.10: Integrated local density of states (LDOS) for the ZnSe VB and CB; ZnSe:Cu Cu$^+$ $e$ and $t_2$ states, and the V$_{Se-2}$ state; and ZnSe:Cu,Al Cu$^+$ $e$ and $t_2$, and Al$^{3+}$ $sp^3$ hybrid orbitals. Atom colors are: Zn (gray), Se (green), Cu (orange), Al (blue).
has two energies, a bonding (V\textsubscript{Se}) and an anti-boding (V\textsubscript{Se}\textsuperscript{*}) configuration. This can be easily seen in the integrated LDOS plots shown in Figure 2.10. Using Gaussian peaks, the bonding orbital is $E\textsubscript{VB} + 1.26$ eV while the anti-bonding state is $E\textsubscript{VB} + 2.19$ eV. For the sake of consistency in measuring the energy spacing between levels, Gaussian peaks were applied with the same FWHM as the Cu related $t_2$ peak. This allows us to measure peak to peak distances which we take to be more consistent than the min, max, or average of a given state or band. The calculated $E_g$ is 2.48eV while the quantum confined experimental $E_g$ is 3.07 eV. Taking the ratio between calculated and experimental $E_g$ as a correction factor, we can assert that the Cu $t_2\leftarrow V\textsubscript{Se}$ energy gap is 1.18 eV (1050 nm), the Cu $t_2\leftarrow V\textsubscript{Se}\textsuperscript{*}$ gap is 2.33 eV (530 nm), and the Cu $t_2\leftarrow CB$ gap is 2.69 eV (460 nm). A labeled diagram with these values can be found in the Figure 2.12 (a). These results confirm that the green PL observed in the emission spectrum is mainly due to the recombination of a hole trapped in the Cu $t_2$ state and the electron from the $V\textsubscript{Se}\textsuperscript{*}$. The $V\textsubscript{Se}$ bonding state apparently acts as an electron trap causing a reduction on potential QY from these systems. It is likely that the Cu$\leftarrow V\textsubscript{Se}\textsuperscript{*}$ and Cu$\leftarrow VB$ both contribute to the green PL peak in these systems, however further discussion is continued supporting the former case below.
Figure 2.11: $d$ orbital DOS for Cu in ZnSe:Cu 64 atom unit cell in a distorted tetrahedral site adjacent to a Se vacancy.

The DOS for the ZnSe:Cu,Al system was studied in a 64 atom super cell by replacing two Zn atoms with a Cu and an Al. Both atoms were distorted in the same direction toward three Se neighbors so the bond distances would be 2.35 Å. The forth Se was distorted toward the Cu and Al with a bond distance of 2.67 Å. The calculated DOS are reported in Figure 2.9 (b) along with the ZnSe DOS, for comparison. As before, the Se 2$p$ and Cu $d(e)$ states are hybridized and make up the VB edge. The Cu $d(t_2)$ states are found at $E_{VB} + 0.45$ eV, similar to the ZnSe:Cu system, as determined by Gaussian fitting. The Gaussian fit peaks and energy level labels can be seen in the supplemental Figure 2.12(b). States associated with Al were found separate and below the CB edge at $E_{VB} + 2.38$ eV. These states were made up of Al sp$^3$ hybridized orbitals. The integrated LDOS are shown in Figure 2.11. Again using the calculated $E_g$ (2.48 eV) and experimental $E_g$ as a correction
factor, the Cu $d(t_2)$←VB transition is expected at 480 nm while the Cu $d(t_2)$←Al is calculated to be 520 nm. These results confirm the DAP recombination mechanism in this system. It is also expected that the ZnSe:Cu,Al will have a slightly blue shifted PL compared to the ZnSe:Cu due to the shallow donor state caused by Al being higher in energy than the $V_{\text{Se}}^*$ state. This result suggests that the emission in

![Figure 2.4](image_url)

**Figure 2.4:** (a) DOS of ZnSe:Cushowing VB and CB edge (red), along with the Gaussian fits for Cu $t_2$ (green), $V_{\text{Se}}$ (light blue), and $V_{\text{Se}}^*$ (dark blue). (b) DOS for ZnSe:Cu,Al including the Al $sp^3$ (light and dark blue), Zn(s), and the Gaussian fit for Cu $t_2$ (green).
the ZnSe:Cu system is due, primarily, to the Cu$\leftrightarrow$V_{Se}$^*$ transition as the ZnSe:Cu,Al PL is blue shifted with respect to the ZnSe:Cu PL.

2.4.8 Time Resolved Photoluminescence

The time resolved PL of ZnSe:Cu and ZnSe:Cu,Al NCs were investigated using TCSPC. The fluorescence decay was monitored following a photoexcitation at 395 nm, which is low enough to minimize initial hot electron relaxation. The PL decay traces were collected over the entire wavelength range of the PL emission peak at a number of individual wavelengths. The time dependence of the normalized emission collected at 530 nm is shown in Figure 2.13(a) for both samples. The PL decay for both samples extends out to 1800 ns, which is orders of magnitude longer than the fluorescence lifetime observed in the host ZnSe.[102] It is evident that the inclusion of Al has a significant effect on the decay by increasing the lifetime of the recombination. To elucidate the effects of Al on the fluorescence process, the single wavelength traces were fit with a triple exponential function, Equation 2.2,

$$I(t, \lambda) = \sum_{i=1}^{3} A_i(\lambda) e^{-t/\tau_i}$$

(2.2)

Where $I(t)$ is the intensity as a function of time $t$, $A_i$ is the initial PL intensity of individual component, $\tau_i$ is the lifetime of that component. The rise component was fit with the instrument response function (IRF) as collected from a scattering sample consisting of a nondairy creamer. The results of the fit are shown in Figure 2.13(a).

The two relatively fast decaying components are similar in both samples, which are 15±1 and 100±10 ns, and attributed to recombination from ST and deep trap (DT) states, respectively. ST states might originate from Se vacancies whereas
Se dangling bonds on the NC surface give rise to DT states.[83] The lifetime for the slow decaying component, which is attributed to dopant related emission, was found to increase from 550±60 to 700±60 ns after Al co-doping. Upon photoexcitation, Al acts as an electron trap whereas Cu acts as a hole trap, giving rise to DAP emission.

Figure 2.5: (a) PL decay traces of ZnSe:Cu and ZnSe:Cu,Al samples collected at 530 nm using a TCSPC system. Each trace required a triple exponential function to achieve good fit that is plotted on top of each decay trace. (b) Spectral deconvolution representing the contribution of various lifetime components to the steady state PL. The integrated PL from each component at each collected wavelength is plotted and fit with Gaussian function.
It is suggested that the efficiency of Al as an electron trap and the spatial proximity of the donor and acceptor levels could be the reason for increased PL QY and lengthened lifetime. However, the elimination of surface Cu and Se vacancies after co-doping could also affect the non-radiative recombination.

The wavelength dependence of the three time constants was examined by taking the lifetimes to be independent of the wavelength, and examining the wavelength dependence of the initial amplitude alone. This procedure was carried out with an in-house written procedure which utilizes singular value decomposition (SVD) to obtain the orthogonal wavelength and time dependent basis vectors, the latter of which is subsequently fit using Equation 2.3 to obtain the wavelength independent time constants reported. The SVD global fitting procedure provides the wavelength dependent initial amplitude, referred to as the B-spectra. To examine the number of photons emitted by a given recombination process, which is directly related to the number of electron hole recombination events produced through a given process, the B-spectra (BS) were integrated with respect to the individual time constants to obtain the photon flux \( \Phi_p \), Equation 2.3 The results of this analysis are shown in Figure 2.13 (b).

\[
\Phi_p(\lambda) = BS(\lambda) \int e^{-t/\tau_i} dt
\]  

(2.3)

The \( \Phi_p \) data corresponding to each spectral component were then fit with a Gaussian function. It is quite obvious from the plot that majority of the emitted photons correspond to the Cu impurity for both samples. Although there is some contribution from ST and DT state emissions (15 and 100 ns components), the ratios
of trap state emissions to that of dopant emission vary considerably among the two samples.

The enhanced QY and decrease in the trap state emission could be explained on the basis of structural and electronic properties as revealed by EXAFS and DFT. In the ZnSe:Cu sample, Cu centers are associated with Se vacancies and ~1/4 of the Cu is on or near the surface of the NC that can lead to non-radiative recombination. Al\textsuperscript{3+} co-doping not only compensates for the charge imbalance originating from Cu\textsuperscript{+} doping, thus eliminating the Se vacancies associated with the Cu center, but also results in enhanced internal doping of Cu. This would lead to a decrease in the density of trap states and trap states related emission, as observed in the time resolved PL data. In addition, Al acts as an efficient electron trap center increasing DAP emission, thereby decreasing the probability of trap mediated non-radiative recombination and leads to enhanced QY.

### 2.5 Conclusions

A wet chemical method was used to synthesize ZnSe:Cu and ZnSe:Cu,Al quantum confined NCs. XRD revealed a zinc blende structure and a particle size around 6 nm, which is further confirmed by TEM. XANES confirms that Cu is in a +1 oxidation state and Al gets incorporated in the vicinity of the Cu site. For ZnSe:Cu NCs, EXAFS supports the existence of two types of Cu sites. One was the interior site where Cu ions occupy an off-centered tetrahedral site accompanying a Se vacancy. This accounts for approximately 3/4 of Cu content, whereas the remaining Cu\textsuperscript{+} occupies a surface site. Co-doping with Al\textsuperscript{3+} results in internal doping, however,
Cu\(^+\) is neither substitutional nor interstitial but occupies a distorted Cu\(_{Zn}\) site close to three of the Se and displaced away from the fourth one. For both samples, the distortion leads to splitting of the second neighbor peak to such an extent that real parts of the FT are no longer in phase, resulting in reduction of amplitude to almost negligible. Fitting the data by including an additional peak around 2.83 Å corresponding to Cu\(_i\)\(^+\) second neighbors, reveals that there is no considerable fraction of Cu\(_i\)\(^+\).

Co-doping with Al was found to increase the QY by a factor of two. Following photoexcitation electrons become trapped at Al donor states, whereas Cu ions act as a hole traps, leading to a DAP recombination. DFT calculations suggest that e \(d\)-orbitals of Cu are strongly hybridized with the VB of the ZnSe NC and \(t_2\) \(d\)-orbitals act as the hole traps after photoexcitation. The efficiency of Al as an electron trap and spatial proximity of the donor and acceptor sites could be the origin of improved QY in ZnSe:Cu,Al. In addition, as revealed by EXAFS, without Al 1/3 of the Cu dopant atoms are on or near the surface that tend to result in trap states that lead to decreased PL. TCSPC studies show that the PL decays follow a triple exponential for both samples. The lifetime constants related to the ZnSetrap states are similar for the two samples, but the lifetime associated with dopant related PL increases from 550 ns in ZnSe:Cu to 700 ns in ZnSe:Cu,Al. The enhancement of PL from co-doping is not only intriguing fundamentally but also opens up new avenues for the potential technological applications of doped semiconductor nanomaterials.
2.6 References


CHAPTER 3: Efficient and Stable Blue to Orange Light Emission from Codoped Core/Shell D$^{3+}$,Cu$^{+}$:ZnSe/ZnS (D=Al, In, Ga) Quantum Dots

3.1 Abstract

Tunable photoluminescence in the visible region has been achieved in ZnSe quantum dots (QDs) through the use of Cu$^{+}$ as a primary dopant and trivalent cations (Al$^{3+}$, Ga$^{3+}$, or In$^{3+}$) as a codopant. While undoped ZnSe QDs emit in the blue and Cu$^{+}$-doped ZnSe QDs emit in the green, introduction of the codopant allows further shift of the PL to yellow and orange, thereby covering most of the visible spectrum. In addition, codoping enhances the PL of Cu$^{+}$, which originates primarily from donor acceptor pair recombination. The PL quantum yield, long term stability, and synthesis process are significantly improved through the use of a ZnS shell and a unique thiol-based bidentate ligand that we developed. The highly monodisperse QDs have an average core diameter of 3.9 ± 0.8 nm and overall particle size of 11 ± 2 nm with the shell included. The locations of the primary dopant and codopants in the QDs were determined by extended X-ray absorption fine structure, where the Cu$^{+}$ ion was found in a distorted tetrahedral geometry whereas the codopant occupied a tetrahedral substitutional site replacing a Zn$^{2+}$ ion in the lattice. Importantly, the codopant was found to stabilize Cu$^{+}$ doping, increasing its incorporation into the ZnSe lattice and thereby its PL yield. To gain deeper insight into the PL properties, density functional theory (DFT) calculations have been carried out, which reveal that the redshift in the PL by adding Ga and In originates from the reorganization of donor and acceptor states within the ZnSe bandgap. In addition, time-resolved PL studies
have found that Cu\(^+\) doping increases the hole lifetime and the codopant creates a stabilizing and localizing center for the electron to subsequently recombine with the hole, resulting in the desired emission. These highly efficient doped ZnSe QDs with stable and tunable PL have great potential for emerging photonics applications in fields including solid state lighting and biomedical imaging.

3.2 Introduction

Semiconductor quantum dots (QDs) nanocrystals (NCs) have been the subject of great interest in the past few decades due to their unique electronic and optical properties that can be tuned by changing the size/shape[1-4] or by doping with other elements,[5-7] resulting in novel functionalities for potential applications in a variety of fields such as LEDs,[8, 9] photovoltaics,[10, 11] biomedical tags,[12, 13] electronics[14] and lasers.[15] Using these QDs as a source of white light emission in solid-state lighting and display applications is an area of intense scientific research.[16] Here, the primary objective is to develop an efficient and economical alternative to conventional light sources, thereby minimizing the global energy consumption and improving the chromophoric quality of display devices. Generally, white light emission is achieved either by red and green phosphors combined with a blue LED as a background, or by using a coated yellow phosphor. More recently, CdS based QDs of three primary colors (blue, green and red) have been employed in LEDs.[9, 17-21] An intrinsic disadvantage of using such a mixture of QDs is the decrease in efficiency due to self-absorption owing to the overlapping absorption and PL spectra. This may result in unwanted changes in the chromophoric coordinates.
affecting the photometric performance. In addition, use of toxic Cd is undesirable from environment safety view point.

One approach to overcome these limitations is to develop doped, wide bandgap semiconductor QDs, such as zinc chalcogenides, with PL covering the visible spectrum. Such doped QDs can be a potential single-emitting component for LEDs based on QD luminophores. In comparison to multiple component systems including both ZnSe and CdSe emitters to cover the visible spectrum, single component system such as ZnSe would have the advantages of cost effective and reproducible methods of fabrication. These doped materials afford the added benefits of minimal self-absorption due to large Stokes shift, longer excited state life times for stronger luminescence, and thermal stability.[22-24] Doping has been employed to introduce defect states into the bandgap of II-VI semiconductors such as ZnSe and ZnS so that photogenerated carriers can relax into donor or acceptor defect states where they can recombine with their photogenerated counterparts, thereby emitting red shifted fluorescence with respect to the bandgap or bandedge emission. Doped II-VI semiconductor QDs have been studied extensively in the past few years, but the possibilities of developing a luminescent material comprising of single host doped QD system with the PL covering most of the visible spectrum have not been less explored. Such QDs can be utilized as excellent optical down-converting materials that would efficiently absorb the high energy photons from the blue light source (such as InGaN LED) used in display devices.
In our previous report,[25] we showed that the introduction of Cu as a dopant to ZnSe QDs could shift its fluorescence from blue to green (~530 nm). With codoping of Al$^{3+}$, along with the Cu$^+$, we could significantly improve the PL quantum yield (QY) by eliminating selenium vacancies ($V_{Se}$) as a consequence of the charge imbalance from Cu$^+$ doping. Also, the Al acted to help localize the photoelectron near the Cu hole acceptor state so that electron hole recombination through the desired donor acceptor pair (DAP) photoluminescent channel was enhanced. However, Al codoped sample still shows emission mainly in green region, and further redshift of the PL is required to make ZnSe a potential candidate for white light solid-state lighting and display applications.
Besides achieving visible PL, high PL yield is another critical factor to consider in doped semiconductor QDs. Since single doping tends to create lattice distortion and/or charge imbalance, codoping has been used as a strategy to reduce lattice distortion and charge imbalance, thereby increasing PL yield. Most co-doping has been conducted by using an oppositely charged element from the primary dopant of similar ionic radius to the host lattice, which together replace the cation and anion of the host semiconductor. This idea is illustrated as a simplified two-dimensional (2D) projection for ease of visualization in Figure 3.1 using ZnSe QDs as a model system. In this example, the Cu$^+$ is the primary dopant and Cl$^-$ is a codopant (bottom left). Doping the host lattice with only Cu$^+$ creates a charge imbalance in the host crystal which can be compensated by doping with a second Cu$^+$ and creating a selenium vacancy ($V_{Se}$) (top right). Consequently, the Cu related emission is reduced due electron recombination channels created by the defect. Alternatively a trivalent cation can be used to replace a Zn$^{2+}$ thereby creating a neutral lattice with Cu$^+$ doping. The use of a codopant that has the same charge as the primary dopant is rare for II-VI semiconductor QDs. As a matter of fact, the use of a trivalent cation (e.g. Al$^{3+}$) as a codopant with a monovalent primary dopant (e.g. Cu$^+$) to replace two neighboring host cations (Zn$^{2+}$ in this example) was the first such strategy developed in our lab, to

**Figure 3.1:** Schematic illustration using a 2D lattice model demonstrating the idea of doping and codoping with opposite and like charged ions as compared to the primary dopant Cu+. Top left: no doping, top right: single doping, bottom left: codoping with oppositely charged ions, and bottom right: codoping with likely charged ions. In this work, D represents Al$^{3+}$, Ga$^{3+}$ and In$^{3+}$.
our best knowledge.[25] In this case, Al codoping was found to increase the PL of Cu but did not alter the emission energy in any significant way.

In this work, we have extended the above strategy to codoping using Ga and In and successfully demonstrate, for the first time, that codoping using Al\(^{3+}\), Ga\(^{3+}\), In\(^{3+}\) can both enhance the PL yield and shift significantly the PL from blue to green and orange, covering essentially most of the visible spectrum (430 nm to 650 nm). The codoped QDs were synthesized using a wet chemistry process. A combination of experimental techniques was used to characterize the structural and optical properties of these QDs. Steady-state and time resolved PL techniques were used in conjunction to probe the underlying photophysical processes. To correlate the optical and structural properties, extended X-ray absorption fine structure (EXAFS) was used to determine the local structure around the dopant and the co-dopant. The results revealed that Cu occupies a distorted tetrahedral site replacing Zn, whereas the co-dopant substitutes a nearby Zn occupying a tetrahedral site, and leads to a decrease in local structural disorder around Cu. In addition, density functional theory (DFT) calculations were performed to gain insight into the nature of various energy levels involved in the optical transitions. With the increase in atomic number of the co-dopant, PL was found to redshift and use of a unique, custom made capping ligand, in conjunction with a ZnS shell, increased the PL quantum yield remarkably.
3.3 Experimental Methods

3.3.1 ZnSe:Cu/ZnSe/ZnS Synthesis

The synthesis of D,Cu:ZnSe used herein was an adaptation from Gul et al.[25] Selenium powder (<325 mesh, 99.7%) was purchased from Acros Organics. Octadecylamine (ODA), diphenylphosphine (DPP), octadecene (ODE), trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), zinc stearate (Zn(St)_2), zinc acetate (Zn(ac)_2), aluminum stearate (Al(St)_3), indium acetate (In(ac)_3), gallium acetylacetonate (Ga(acac)_3), sulfur powder, methanol (MeOH), isopropyl alcohol (IPA), and dichloromethane (DCM) were purchased from Sigma Aldrich. Anhydrous reagents should be used. Lipoic acid (LA) was purchased from Alfa Aesar. Five solutions were prepared in a dry N_2 glove box herein referred to as ‘A,’ ‘B_{Cu,D},’ ‘C,’ ‘D,’ and ‘main’. Solution A contained 0.028 g Se (355 µmol), 0.2 g ODA (740 µmol), and 0.18 g DPP (970 µmol) which was sonicated with mild heating (40 °C) until the Se was dissolved. It should be noted that heating DPP much above 50 °C can be very dangerous and special care should be taken as the vapor will readily permeate under Teflon lined septa and dissolve rubber caps. Solution B_{Cu,Al} contained 0.01041 g Cu(ac)_2 (57.3 µmol), 0.0504 g Al(St)_3 (57.4 µmol), 3.70 g ODE, 0.2 g TOPO, and 0.02 g ODA. TOPO and ODA aided in solubility. Solution B_{Cu,Ga} contained 0.01029 g Cu(ac)_2 (56.7 µmol), 0.02104 g Ga(acac)_3 (57.3 µmol), 3.70 g ODE, 0.22 g TOPO, and 0.20 g ODA. Solution B_{Cu,In} contained 0.01041 g Cu(ac)_2 (57.3 µmol), 0.01699 g In(ac)_3 (58.2 µmol), 3.70 g ODE, 0.32 g TOPO, and 0.20 g ODA. Solution B_{Cu} contained 0.0106 g Cu(ac)_2 (58.4 µmol), 3.70 g ODE, 0.22 g
TOPO, and 0.20 g ODA. Solution C contained 0.90 g Zn(st)$_2$ (1,400 µmol), 0.20 g ODA (740 µmol), 1.5 g TOP (4,000 µmol), and 7 g ODE. Heating was required to achieve solubility for some B$_{Cu,D}$. Solution D contained 0.0343 g S (1,070 µmol), 0.2 g DPP (1,070 µmol), 0.1 g ODA (370 µmol), and 8 g ODE. Solution D was also sonicated and mildly heated with solution A to dissolve the S powder. Because the DPP was dispersed in a significant quantity of ODE in D, the dangers seen in A were not observed and heating up to 120 °C was not a problem. Finally the ‘main’ pot contained 0.018 g Zn(ac)$_2$ (100 µmol), 7.9 g ODE, and 0.05 g TBP (250 µmol).

In a typical reaction, a Schlenk line with N$_2$ and rough pump with liquid nitrogen (L-N$_2$) trap (40 mtorr minimum) was utilized. A 100 mL three neck round bottom flask, with condenser, thermocouple, and septa was evacuated for 12 hours prior to the reaction. After purging with dry N$_2$, the solution ‘main’ was added to the RB flask. This solution was evacuated for a minimum of 30 minutes, followed by three purge/pump cycles. The solution was heated to 100 °C with two more purging/pump cycles. The main flask was then heated to 300 °C upon which solution A was injected rapidly with very fast stirring and an instant color change to pale yellow was observed. Heating between 280 and 300 °C was maintained for 60 seconds upon which the temperature was rapidly quenched with forced air to 180 °C. The solution may become turbid at this point. This temperature was allowed to stabilize prior to the drop-wise addition (1 drop per 30-60 sec.) of 175 µL B$_{Cu,D}$. After 10 minutes the mixture was heated to 240 °C and maintained for 1-3 hours.
A ZnSe over layer on the now surface doped ZnSe NCs was done at the same temperature by adding 250 µL of C, solution C was maintained independently at ~100-120 °C under N₂ to keep the solution dissolved. During the addition the injection needle was also heated with a heat gun toward the reaction flask to keep the solution dissolved during the addition. The 250 µL of C was added drop-wise over the course of 60 sec while maintaining vigorous stirring. This was allowed to react for 1 hour whereupon an additional 250 µL was added. In 30 minute intervals solution C was added in 250 µL volumes until the main pot became clear yellow which was related to excess Zn in solution from the total Zn added. An additional 1 mL of C was added at this point to drive the Zn concentration up in the main pot.

A ZnS shell layer was added on top of the now ZnSe: Cu/ZnSe NCs through the cycled addition of D and C over the course of 2 hours at a temperature maintained between 220-240 °C. A typical addition was 1-2 mL of D with 15 minutes wait, 1-2 mL of C with 15 minutes wait. Slower additions were taken to be better but 2 mL injections also produced quality particles. The addition of both D and C should be done drop-wise to keep from nucleating new particles. After finishing the addition of D and C, there may be ~1-2 mL of D left over but the main pot should be clear, the mixture was maintained at 240 °C for 30 minutes. The temperature was dropped to 220 °C where the capping ligand mixture was added drop-wise. The synthesis of the capping ligand is described below. After the addition of the capping ligand, the reaction was cooled slowly to room temperature.
The undoped ZnSe NCs were prepared in the same fashion as described above except there was no addition of B. Otherwise, all steps were identical.

The crude reaction mixture was cleaned with liquid/liquid extraction with a mixture of MeOH and DCM. The extraction was achieved by adding the main pot mixture to a 250 mL separatory funnel then adding a volume of MeOH (~50-100 mL). The main pot mixture was denser than the MeOH layer, so DCM was added until an inversion was achieved (~10 mL). The DCM has the added benefit of improving the separation. This process was continued until the MeOH/DCM layer was no longer turbid. A gradual increase in the MeOH/DCM ratio toward the end improved the removal of ODE and concentrating the NCs. When the final ODE/NC layer was lowered to ~1-2 mL, a final rinse was done by floating the NC layer on the MeOH/ODE than adding a small amount of IPA. The resulting crystals solidified and could be collected by centrifuge and were finally dried under a stream of argon and stored.

3.3.2 Capping Ligand Synthesis

The capping ligand was synthesized fresh every time alongside the NCs. In a N₂ glove box a solution was prepared containing 0.1469 g LA, 0.2639 g TOP, and 0.1907 g oleylamine. The mixture was placed in a 25 mL three neck round bottom flask connected to the Schlenk line and degassed for 10 minutes with 3 pump/purge cycles with dry N₂. The reaction was heated with stirring to 120 °C and maintained for the totality of the NC synthesis (~16 hours). The reaction color changed from yellow to clear which indicated the cleavage of the disulfide bond.
3.3.3 Steady State Optical Characterization

The room temperature optical absorption spectrum of the NCs dispersed in DCM was recorded with a Hewlett Packard 8452A diode array spectrometer. The room temperature photoluminescence spectrum was recorded using a Perkin-Elmer Luminescence spectrometer.

3.3.4 Time Resolved Fluorescence

Time resolved PL of ZnSe, ZnSe:Cu, ZnSe:Cu,Al, ZnSe:Cu,Ga, and ZnSe:Cu,In core shell NCs was performed with time correlated single photon counting (TCSPC) at room temperature using a system and techniques described elsewhere. [25, 26] Briefly, a 200 MHz Ti:sapphire laser (tunable 790-820 nm) with an output of 350 mW, was passed through a Conoptics pulse picker to select a 500 KHz pulse train and a BiBO to for to generate the second harmonic. This ~405 nm centered, 4 µJ, laser was used to excite the sample. The fluorescence light from the sample was collected tangentially to the excitation laser and passed through a monochromator with 0.25 nm resolution. Detection was achieved with an ID100 avalanche photodiode (IDQ, Switzerland). The instrument response function was determined to be 50 ps, as determined from scattering of the excitation light from a non-dairy creamer solution. Data was analyzed with IGOR Pro (wavemetrics) as well as singular value decomposition global fitting procedures developed in-house for Matlab.
3.3.5 Computation

Calculations on ZnSe, ZnSe:Cu, ZnSe:Cu,Al, ZnSe:Cu,Ga, and ZnSe:Cu,In were performed with the PWscf package contained in the Quantum ESPRESSO code.[27] Density function theory (DFT) calculations were performed with the PBE functional and ultra-soft pseudo-potentials on a super cell containing 64 atoms for ZnSe, ZnSe:Cu,Al, ZnSe:Cu,Ga, and ZnSe:Cu,In and 63 atoms for ZnSe:Cu$_2$. The optimized unit cell parameter (a) was 5.74 Å. For ionic position optimization, damp dynamics were used with a 4x4x4 K point mesh. The Cu-Se bond distances were constrained to the experimentally determined bond distances from EXAFS, as PBE was not able to duplicate the experimental lattice position of Cu, while the remaining atoms were allowed to vary. SCF and NSCF calculations were performed with kinetic energy cutoff of 70 Ry for wavefunctions and 700 Ry for the charge density, a 8x8x8 K point mesh, and tetrahedral occupations. The local density of states (LDOS) were calculated with projwfc.x.

3.3.6 EXAFS

X-ray absorption measurements at the Cu, Zn and In K-edges were performed at the Stanford Synchrotron Radiation Lightsource (SSRL), on beamline 7-3 at 10 K. The monochromatized radiation from a Si (220) double crystal monochromator was detuned to 50% of its maximum at the metal K-edge to minimize the effects of higher harmonics. The beam size on the sample was reduced to 0.5 mm vertical and 1.0 mm horizontal FWHM. In case of In K-edge, intensity of the incident x-rays ($I_0$) was monitored by Ar filled ion chamber in front of the sample, whereas $N_2$ was used for
other measurements. Along with the samples, respective metal foils were measured during each scan using a reference ion chamber to calibrate the energy scale. Zn data was collected in transmission mode, while Cu and In measurements were carried out in fluorescence mode using a 30 element Ge detector (Canberra). QD samples were deposited in plexiglass sample holders with kapton film windows.

All data were processed using standard programs based on IFEFFIT.[28, 29] After calibrating the energy, individual scans were averaged together to improve the signal to noise ratio. Athena software was used for background removal and extraction of EXAFS oscillations $\chi(k)$ as a function of photoelectron wavenumber $k$. The extracted $k$-space data, $k^3\chi(k)$, was then used to FT the data into r-space. Theoretical EXAFS models were calculated using FEFF6[30] and fitting program Artemis was used for fitting the data. In theoretical EXAFS signal, variable parameters included the passive electron reduction factor ($S_0^2$), the bond distance between the absorbing atom and its nearest neighbors ($R_j$), mean square displacement of the bond distance ($\sigma^2$), and the co-ordination number ($N_j$) of the nearest neighbors around the central atom. In case of each element, the value for ($S_0^2$) was determined from the fits to the respective reference metal foils’ data, and was fixed during the fits. Other parameters ($N, R, \sigma^2$) were allowed to vary and fine tuned during the fitting process.
3.4 Results and Discussion

3.4.1 Optical Properties of the Codoped Quantum Dots

Optical properties of the QDs were investigated with both electronic absorption and PL spectroscopy. Shown in Figure 3.2 is the UV-Vis spectra of ZnSe/ZnS, ZnSe:Cu/ZnS, ZnSe:Cu,Al/ZnS, ZnSe:Cu,Ga/ZnS, and ZnSe:Cu,In/ZnS core/shell QDs. Also indicated is the bandgap for bulk ZnSe and the Gaussian fit of the absorption edge of the QDs. The absorption spectra have been offset for clarity. The absorption onsets of all the samples occurred at the same energy, 2.97 eV (417 nm), demonstrating the high degree of uniformity from batch to batch. The absorption edges were blue shifted from that of bulk ZnSe, which has a bandgap at room temperature of 2.70 eV (460 nm),[31-33] as a result of quantum confinement in the ZnSe core. ZnS has a bulk bandgap of 3.68 eV (337 nm) which is significantly blue shifted of the absorption edge of ZnSe and as such is not observed in the recorded absorption spectrum of the core/shell quantum dots. The bandgap (E\text{g}) transition in ZnSe is a charge transfer from Se to Zn and is direct and dipole allowed. Also, no change in the absorption edge was seen with the inclusion of the dopant (Cu) or codopants (Al, Ga, or In).
The PL spectra from the five systems studied are shown in Figure 3.3 along with a photograph of the cleaned samples as excited by a UV light. It is relevant to mention that typically cleaning ZnSe QDs from their crude reaction mixture can be quite challenging and often results in quenching of the PL. Here however, these QDs had been washed several times, crashed, and stored prior to being re-suspended in chloroform which marks a significant advancement in ZnSe QDs. The manner in which this was accomplished is discussed in further detail below.

The blue emitting ZnSe/ZnS has a prominent emission centered at 437 nm with some asymmetric tailing into the red. Gaussian fitting of this feature resulted three peaks 434 nm, 446 nm, and 463 nm with FWHM of 10, 12, and 18 nm respectively. The 434 nm (2.86 eV) emission, related to the conduction band minimum (CBM) to valence band maximum (VBM) transition, is higher in energy than the bulk bandgap (2.70 eV) as a result of quantum confinement. Compared to the absorption edge measurement of the bandgap (2.97 eV) the exciton binding
energy is approximately 110 meV which is consistent with previous reports in quantum confined CdSe.[34] The quantum confinement seen is consistent with the size of the ZnSe core size measured by TEM herein and the Bohr exciton radius of bulk ZnSe, reported to be 4.5 nm.[32] The two other peaks observed in this sample are related to defect emission.

The ZnSe:Cu/ZnS sample required 4 peaks to fit the PL spectrum which were 436 nm (2.84 eV), 448 nm (2.77 eV), 514 nm (2.41 eV), and 580 nm (2.14 eV) with FWHM of 10, 10, 44, and 33 nm, respectively. The 514 nm emission is assigned to Cu^{2+}←CBM and the difference in energy between the CBM←VBM transition and the Cu emission results in a Cu acceptor state located at VBM + 0.43 eV. The additional peak at 580 nm, which accounts for the red tailing of the Cu emission, suggests that the Cu site is more distorted in this sample compared to the ZnSe:Cu,Al/ZnS, for example. This 580 nm transition is attributed to DAP recombination between the photogenerated Cu^{2+} and a donor state at CBM – 0.28 eV. As Cu dopes the ZnSe lattice as a +1 ion at a Zn^{2+} site, as determined by XANES,[25] charge balancing the lattice requires a second Cu^{+} to dope near the first and a selenium vacancy (V_{Se}^{2−}) to be created. This results in a neutral charge in the NC however the V_{Se} introduces a dangling bond defect within the NC and next to the Cu center. This V_{Se} related state can be associated to the 580 nm emission which places the V_{Se} donor state at CBM – 0.28 eV.

For ZnSe:Cu,Al/ZnS three peaks were required to fit the PL emission: 432 nm (2.87 eV), 446 nm (2.78 eV), and 509 nm (2.44 eV) with FWHM of 10, 10, and 45
nm, respectively. The appearance of the 509 nm emission is attributed to the addition of Cu$^+$ which acts to trap the photohole, generating an intermediate Cu$^{+2}$. The photoelectron can decay via two major pathways, either to a hole in the VBM, resulting in 432 nm emission, or to fill the Cu$^{+2}$ photohole causing the 509 nm emission. The difference in energy between the $E_g$ and the Cu related emission is 0.43 eV. This suggests the Cu acceptor state is located at VBM + 0.43 eV. The significant amount of bandgap emission in this sample also suggests that the donor state introduced by Al$^{+3}$ is at or near the CBM such that a photoelectron localized near the photohole trapped at Cu is less likely thereby decreasing DAP recombination.

Low temperature (2K) studies place the donor level of Al, Ga, and In in ZnSe at 18.35, 20.26, and 21.03 eV, respectively.[35] While the values of the donor levels at room temperature are expected to be different, as is the case with the bulk bandgap which is 2.81 eV at ‘0K’ and 2.70 eV at RT,[33] the trend is expected to be conserved.

With Ga co-doping, the PL in this system was shifted significantly to the red, compared to the previously discussed samples, causing a very clean yellow emission. The $E_g$ emission seen in the previous samples was completely eliminated. Two peaks were required to fit the PL spectrum at 541 nm (2.29 eV) and 599 nm (2.07 eV), with FWHM of 45 and 40 nm, and which represented 82 and 18 % of the integrated area of the emission peak, respectively. Taking the energy level of the Cu acceptor state to be unaffected by the addition of Ga$^{+3}$, at least to a first approximation, the red shift of the PL can be ascribed due to an acceptor state from Ga. This donor state is located at CBM – 0.14 eV and the primary emission seen at 542 nm is therefore due to DAP
recombination between the photogenerated species: \( \text{Cu}^{+2} \leftarrow \text{Ga}^{+2} \). Effective localization of the photoelectron into the \( \text{Ga}^{+3} \) acceptor state is responsible for the elimination of the \( E_g \) emission in this sample. The red tailing represented by the second peak at 599 nm can be assigned to defect related emission caused by imperfect doping, i.e. doping a Ga in the a lattice position greater than the second neighbor shell from Cu can reduce the effectiveness of the DAP recombination channel and the benefits of neutralizing the lattice charge imbalance by reducing \( V_{\text{Se}} \) formation.[25] Alternatively, the red tailing can also be due to Ga:ZnSe which has been reported to have bulk emission centered around 600 nm.[36]

Finally, In co-doping with Cu has the largest red shift of all the samples studied and appeared orange by eye under UV illumination. Again, the PL spectrum also shows no evidence of \( E_g \) related emission. Fitting of the spectrum resulted in two peaks at 562 nm (2.21 eV) and 609 nm (2.03 eV), with FWHM of 43 and 52 nm, and which represented 66 and 34% of the total integrated area of the emission, respectively. The donor state related to In, again assuming the Cu state is constant at VBM + 0.43 eV, is at CBM – 0.22 eV. Additional red tailing, represented by the 609 nm peak, was seen with respect to the previous ZnSe:Cu,Ga sample which can be attributed to defect states caused by the relatively large In ion at the Zn site. The In ion, as will be discussed in the EXAFS section, was seen to distort the nearest neighbor shell by 0.1 Å compared to the pure ZnSe NCs. By DFT modeling, also discussed in further detail below, the In – Se bond distance was found to be 2.642 Å,
whereas the Ga–Se, Al–Se, and Zn–Se bond distances were 2.481 Å, 2.456 Å, and 2.454 Å, respectively.

It should be noted that trials with Cu and Tl were attempted with little success although some red PL was observed in one sample, albeit weak. Tl is significantly larger than In, which already places strain on the lattice to fit, and is less likely to as a result to be accepted by the host ZnSe lattice. Further studies are needed however to fully explore this possibility which, as will be discussed further in the computational section, has the potential for shifting the PL into the red. These exciting results suggest a clear alternative to CdSe quantum dots for next generation LEDs where the

![Photoluminescence (PL) of ZnSe (blue), ZnSe:Cu,Al (light blue), ZnSe:Cu (green), ZnSe:Cu,Ga (yellow), and ZnSe:Cu,In (orange).](image)

Figure 3.3: Photoluminescence (PL) of ZnSe (blue), ZnSe:Cu,Al (light blue), ZnSe:Cu (green), ZnSe:Cu,Ga (yellow), and ZnSe:Cu,In (orange).
use of Cd offers clear disadvantages from a human health and environmental impact perspective.

While the first approximation of the Cu acceptor levels by assuming the acceptor states are constant with respect to the VBM is convenient to establish the donor level with respect to the CBM, it does not tell a complete and accurate story.

As will be discussed in more detail below, the Cu local structure is strongly affected by the identity of the codopant insofar as the codopant will change the nearest neighbor Cu-Se bond distance. For instance, Ga doping causes the Cu to occupy a less disordered site than In or Al. DFT modeling of the donor site, also discussed below, places the In and Ga donor states at the same place in the host lattice. As a

**Figure 3.4:** Summary of the electronic energy levels of ZnSe doped with Cu+ and co-doped with Al+3, Ga+3, or In+3.

As will be discussed in more detail below, the Cu local structure is strongly affected by the identity of the codopant insofar as the codopant will change the nearest neighbor Cu-Se bond distance. For instance, Ga doping causes the Cu to occupy a less disordered site than In or Al. DFT modeling of the donor site, also discussed below, places the In and Ga donor states at the same place in the host lattice. As a
result, we can conclude that there is a coupled effect of donor and acceptor state locations within the host lattice which the remainder of this paper will attempt to elucidate.

To summarize, the energy levels of the donor and acceptor states discussed above are provided in Figure 3.4, assuming a constant Cu acceptor level which is not entirely the case. The observed bandgap also indicated, $E_g = 2.97$ eV, and the energy levels are provided with respect to their location to either the VB or CB as indicated. The extent of tunability of these states by quantum confinement has not been fully examined at this point. It is likely that the donor and acceptor states will remain at relatively the same levels with respect to the CB or VB as the $E_g$ is widened by quantum confinement.

3.4.2 Structure and Morphology

The size and shape of the QDs were studied with transmission electron microscopy (TEM). All five core/shell QD samples (ZnSe/ZnS, ZnSe:Cu/ZnS, ZnSe:Cu,Al/ZnS, ZnSe:Cu,Ga/ZnS, and ZnSe:Cu,In/ZnS) exhibited the same general size and shape. A representative low resolution TEM image is shown in Figure 3.5 (a) and a high resolution image shown in Figure 3.5 (b) for ZnSe/ZnS. In the low resolution image, the QDs were primarily triangular plate in shape with the thickness of the plate measured to be $11 \pm 2$ nm. A darkened circle in the center of a majority of the triangles was observed, which has a $3.9 \pm 0.8$ nm diameter. By high resolution TEM (HRTEM), the core/shell structure of the QDs can be seen as two distinct lattice
spacings of 3.3 and 3.1 Å were seen for ZnSe and ZnS, respectively, consistent with the (1 1 1) d-spacing of the zinc blende crystals. The region outlined in red indicates the region containing the core. These images show a significant fraction of the quantum dots are composed of ZnS as thick shells over the ZnSe cores. This result was intended as a large excess of ZnS was introduced during the growth of the QDs in an effort to improve core insulation. A simplified schematic representation of the QDs is presented in Figure 3.5(c) indicating the overall core is primarily triangular growths off crystal facets of core ZnSe. Local structure of dopant atoms within the host lattice

Figure 3.5: (a.) Low resolution image of ZnSe/ZnS core/shell QDs. (b.) HRTEM image indicating the ZnSe core outlined in red and the triangular growths of the ZnS shell. (c.) A cartoon representation of hexagonal core with triangular shell.

3.4.2.1 Cu Local Structure

EXAFS is a unique technique capable of resolving bond distances with angstrom resolution for specific atomic species within a heterogeneous structure. By probing the x-ray absorption for a specific element past the initial onset of absorption edge, photoelectrons are generated from the probe atom which attempt to leave the emitter atoms as a spherical wave. The electron wave front, as it moves away from
the emitter atom, can reflect off the electron cloud of the neighboring atoms and consequently the forward and reverse traversing wave will interfere. This interference will depend strongly on the wavelength of the electron (i.e. its kinetic energy) as well as the neighboring atom distance. Because the probability of the emitter atom to absorb a photon depends on the initial and final state wavefunctions, if the interference is constructive then the probability of absorption increases, conversely if interference is destructive the probably will decrease. Because the neighboring atom distances are fixed, an observation of the absorption intensity as a function of photoelectron kinetic energy (varied with the incident x-ray photon energy), the resulting oscillations in the absorptivity can be recorded and extracted through fitting and Fourier transform (FT). These data can provide detailed bond distance information for neighbors up to three shells away for a highly crystalline material. Less orderly crystals or amorphous solids will typically only resolve the first shell.

For the ZnSe:Cu,D NCs, the extracted EXAFS oscillations in $k$-space were FT into $r$-space to get the structural information. The $r$-space traces for all the samples are shown in Figure 3.6 (a). Zn $K$-edge EXAFS is also plotted to compare with the Cu data because if the Cu simply replaced a Zn atom in the lattice, the EXAFS should be very similar and easily comparable. The peaks correspond to the distances between the absorbing Cu and the neighboring atoms, after correcting for the photoelectron phase shift, which results in shifting the peak position to shorter distance by ~0.4 Å.[37] In cubic ZnSe, Zn is tetrahedrally coordinated by 4 Se atoms which are at 2.45 Å.
Å, and the corresponding peak in EXAFS data appears at apparent distance of ~2.1 Å. The second peak around 3.65 Å and third peak at 4.40 Å originate from the 12 Zn second neighbors and 12 Se third neighbors, which are at a distance of 4.01 and 4.70 Å, respectively.

Cu can either occupy a Zn substitutional site, or occupy a tetrahedral interstitial site where the 4 nearest neighbors (Se/Zn) would be at 2.45 Å and 6 second neighbors (Se/Zn) would be at 2.83 Å, as shown in Figure 3.6 (b). The absence of any peak close to 2.5 Å in Cu EXAFS data (corresponding to second neighbor distance 2.83 Å) rules out the possibility of Cu occupying a tetrahedral interstitial site. Also, based on the first principle calculations, Liang et al. has shown that Cu site involved in the dopant emission cannot be the interstitial tetrahedral one as Cu 3d impurity band would lie deeper in the valence band of the host.[142] Another possible interstitial site, represented in Figure 3.6 (c), is hexagonal (or octahedral) where Cu is surrounded by 6 neighbors (3 Se and 3 Zn atoms) at 2.35 Å, in which Cu cation might lead to a slight polarization of the lattice causing the Se anions to move slightly closer while Zn cations a little outward. However, occupying such an interstitial site would yield a second neighbor peak at an apparent distance of ~3.3 Å (corresponding to 4 Zn and 4 Se second neighbors at 3.68 Å). The absence of any prominent peak around 3.3 Å in the r-space data renders the occupation of this site unlikely. This site can also be ruled out through examination of the DOS in which the Cu d states do not contribute acceptor levels within the bandgap and is thus
not consistent with the PL in ZnSe:Cu, these results are discussed in additional detail below.

In the Cu EXAFS the first peak appears at approximately 0.1 Å shorter distance than the Zn trace. In our previous study, Cu was found to occupy a distorted tetrahedral site, where 3 Cu-Se bond distances are shorter than the fourth one.[25] In the +1 oxidation state it is not unusual for Cu to occupy a distorted tetrahedral site as seen in Cu$_2$Se[39] and CuSe.[40] Therefore, we believe that Cu$^+$ occupies a substitutional Zn site where it resides in a defect tetrahedral environment of 4 Se as seen in Cu$_2$Se and CuSe.

Visual examination of the Cu traces (Figure 3.6 a) depicts that the second and third neighbor peaks are quite prominent in the case of ZnSe:Cu,Ga (highlighted by a rectangle). Although, these peaks are noticeable in ZnSe:Cu,Al, they are not evident in the ZnSe:Cu and ZnSe:Cu,In samples. This suggests that the size of the co-dopant affects the degree of disorder around the dopant. Being a neighboring element, the size of Ga is comparable to that of Zn and Cu, and results in the least disorder around the dopant. This observation also supports the suggestion that in ZnSe:Cu a Se vacancy accompanies the dopant.[25] Otherwise, Cu with a similar size as Zn, would not result in a more distorted structure leading to the absence of second neighbor peak. The effect of the codopant on the local structure of Cu further suggests that the codopant enters the host lattice in the vicinity of the dopant.

To further extract the structural information fitting was performed, in which case theoretical EXAFS parameters were calculated using FEFF6 starting with cubic
Figure 3.6: (a) Magnitude of the Fourier transform of Cu EXAFS functions (k^3\chi) in ZnSe:Cu (green), ZnSe:Cu,Al (blue), ZnSe:Cu,Ga (black), and ZnSe:Cu,In (light blue) along with ZnEXAFS for ZnSe (red). In case of ZnSe:Cu,Ga, and ZnSe:Cu,Al, the peaks corresponding to the second and third shell neighbors have been highlighted using a rectangle. (b) Tetrahedral interstitial site showing Cu surrounded by 4 nearest neighbor Se atoms at 2.45 Å. The impurity atom was placed at ([1/2, 1/2, 1/2]*a), where a = 5.6676 Å. (c) Hexagonal interstitial site where Cu has 3 Zn and 3 Se nearest neighbors at 2.35 Å. Here Cu was positioned at ([3/8, 3/8, 5/8]*a). (d) First shell fits (red) to the r-space data of Cu EXAFS for all the four samples.

ZnSe and replacing the central Zn with Cu. However, in all the samples a Cu-S path has to be included to fit the data, which indicates that some of the Cu is either present on the surface of ZnSe core or enters the ZnS shell. The latter case is not an
unreasonable conclusion considering the synthesis was completed in one pot and residual Cu in the crude pot is likely. The best fits obtained for the first shell using a two phase system are shown in Figure 3.6 (d) along with the data. As more than one phase existed leading to multiple shell contributions, a variable parameter $x$ was introduced into the EXAFS equation used by Artemis program of IFEFFIT package, such that

$$
\chi_{total}(k) = \sum_i x_i \chi_i(k) \quad (3.1)
$$

Where $x_i$ is the individual contribution of each phase and $\chi_i(k)$ is the EXAFS function of each individual phase. Since the roles of $x_i$ and the coordination number ($N_j$) would be complementary, the coordination number for each phase was fixed while $x$ was used as a variable parameter during the fitting process. The uncertainty in $x$ was estimated to be around 10%. The structural parameters extracted from the best fit results have been reported in Table 3.1. In the ZnSe:Cu sample, the Cu-Se distances were 2.35 Å (which is shorter than 2.45 Å, the Zn-Se distance), whereas Cu-S distances were 2.25 Å (shorter than 2.34 Å, the Zn-S bond length). These results are consistent with the previous reports,[104, 117, 134] suggesting that Cu occupies a distorted tetrahedral site by replacing Zn. Only 1/3 of the Cu had Se nearest neighbors with the remaining Cu having S nearest neighbors. The addition of Al as a codopant increase the fraction of Cu associated with the core ZnSe to 51%. Doping with Cu$^+$ in ZnSe must occur by replacing two Zn atoms with Cu$^+$ and creating a $V_{Se}^{-2}$. The inclusion of Al$^{+3}$, also at a Zn site, allows for the addition of one
Cu atom without creating a vacancy. The result is increased solubility in the lattice and increased Cu content in the core.

**Table 3.1:** Local structure parameters for In and Cu in nanocrystal samples determined from the best fits of Fourier transformed data. Debye-Waller factor ($\sigma^2$) was used as a variable parameter whereas $S_0^2$ value was fixed to 0.83 for Cu and 0.94 for In data. Structural parameters for bulk ZnSe have also been listed in the beginning.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Path</th>
<th>R (Å)</th>
<th>N</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\chi^2$ (%)</th>
<th>R-factor</th>
<th>$\chi^2_{\text{red}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe Bulk</td>
<td>Zn-Se</td>
<td>2.45</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn-Zn</td>
<td>4.01</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn-Se</td>
<td>4.70</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnSe:Cu,In (In EXAFS)</td>
<td>In-Se1</td>
<td>2.55±0.003</td>
<td>4.0±0.3</td>
<td>0.002±0.0003</td>
<td>0.003</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In-Zn</td>
<td>4.03±0.02</td>
<td>9.3±0.4</td>
<td>0.007±0.002</td>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>In-Se2</td>
<td>4.66±0.01</td>
<td>7.9±0.4</td>
<td>0.009±0.005</td>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnSe:Cu</td>
<td>Cu-Se</td>
<td>2.35±0.01</td>
<td>3</td>
<td>0.009±0.004</td>
<td>34</td>
<td>0.0002</td>
<td>405</td>
</tr>
<tr>
<td></td>
<td>Cu-S</td>
<td>2.25±0.01</td>
<td>3</td>
<td>0.002±0.001</td>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnSe:Cu,Al</td>
<td>Cu-Se</td>
<td>2.37±0.02</td>
<td>4</td>
<td>0.017±0.003</td>
<td>51</td>
<td>0.0007</td>
<td>474</td>
</tr>
<tr>
<td></td>
<td>Cu-S</td>
<td>2.25±0.01</td>
<td>4</td>
<td>0.001±0.0008</td>
<td>49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnSe:Cu,Ga</td>
<td>Cu-Se</td>
<td>2.39±0.01</td>
<td>4</td>
<td>0.007±0.001</td>
<td>60</td>
<td>0.0006</td>
<td>351</td>
</tr>
<tr>
<td></td>
<td>Cu-S</td>
<td>2.27±0.01</td>
<td>4</td>
<td>0.006±0.002</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnSe:Cu,In</td>
<td>Cu-Se</td>
<td>2.38±0.01</td>
<td>4</td>
<td>0.003±0.001</td>
<td>53</td>
<td>0.0007</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td>Cu-S</td>
<td>2.27±0.01</td>
<td>4</td>
<td>0.007±0.002</td>
<td>47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A *k*-space range of 2.5 < $k$ (Å$^{-1}$) > 14 was used for In EXAFS, whereas a *k*-space window of 2.5 < $k$ (Å$^{-1}$) > 11.5 was used for Cu EXAFS data.
Also, a slight lengthening of the Cu-Se bond distance was observed in ZnSe:Cu,Al which increased to 2.37 Å. This suggests that the tetrahedral environment around Cu is less distorted as compared to the sample without the codopant. For ZnSe:Cu,Ga the Cu-Se distance was found to be 2.39 Å which again closer to that for perfect tetrahedral site (2.45 Å). Also, the solubility of Cu in ZnSe:Cu,Ga increased slightly to 60% of Cu in the core. We attribute these effects to smaller lattice distortions due to comparable sizes of Zn, Cu and Ga. The percentage of Se nearest neighbors in ZnSe:Cu,In decreased slightly as compared to Ga codoped sample, and was comparable to ZnSe:Cu,Al. This could be due to the larger In size leading to increase in lattice strain. This is further discussed in the following section.

3.4.2.2 In Local Structure

Studies of the codopant by EXAFS is made challenging by a number of overlapping features in XAS. The Al K-edge X-ray absorption is overlapped by the Se L$_1$-edge and in the case of Ga the overwhelming fluorescence signal from Zn makes it impossible to measure the XAS spectrum of Ga using fluorescence yield. Consequently, In was the only option to probe the local structure of the co-dopant in these samples. The FT of $k^3$-extracted EXAFS signal for In is shown in Figure 3.7 (a) along with that of Zn for comparison. It is quite clear from the shape of the FT that In is occupying a Zn substitutional site. However, the first peak for In appears at a slightly longer distance (approximately by 0.1 Å) as compared to Zn.

To extract the structural parameters, EXAFS fitting analysis was conducted starting with cubic ZnSe as a model compound and replacing the central Zn with In.
A fit was then carried out over an r-space range of 1.78-4.75 Å using three single scattering paths corresponding to In-Se1, In-Zn and In-Se2. The best fit generated is shown along with the data in Figure 3.7 (b). The fit agrees very well with the experimental data indicating the reliability of the used structural model and accuracy of the fit. The inter atomic distances and the corresponding EXAFS Debye-Waller factors are represented in Table 3.1 including the other statistical parameters. The In-Se1 pair distance was longer than that of Zn-Se1 by 0.1 Å (2.55 instead of 2.45 Å).

Because of the larger ionic size of In compared to Zn, the Se atoms are pushed to longer bond distances as it occupies more volume in the host lattice. Likewise, an increase in the second neighbor distance was seen but not as pronounced (0.02 Å), whereas a decrease of 0.04 Å was observed for third neighbor distance. Though the changes in case of second and third neighbor distance are small and within the error
range of this technique, but indicate small changes in the dihedral angels involved. This result speaks to the power of EXAFS in measuring precise interatomic bond distances such that the very small change in the bond distances between In and Se can be clearly resolved compared to Zn and Se.

### 3.4.3 Density of States from DFT Calculations

To further understand the origin of the PL from the NCs as a consequence of doping and codoping, density functional theory was applied to a 64 atom ZnSe super cell as a model system. The cubic super cell was previously optimized to obtain a unit cell parameter $a = 5.67 \text{ Å}$. To this unit cell, one Zn was replaced with Cu and the bond distances from Cu to three of the nearest Se atoms was fixed to the bond distance as found from EXAFS ($\text{Cu} - \text{Se} = 2.36 \text{ Å}$). A second Zn directly adjacent to the Cu was replaced by the D atom (D = Al, Ga, In, or Tl) in the case of the donor systems. For the ZnSe:Cu system, a second Zn was replaced by a Cu and the co-shared Se atom was removed; by doing so the crystal would remain charge neutral as Cu is +1 in the lattice, and replacing two Zn$^{+2}$ would leave the crystal overall with a -2 charge. Compared to our previous study,[25] all lattice ion positions were optimized with the exception of the constraint on the Cu-Se bond distance. The reason being that PBE was not able to correctly predict the defective Cu-Se bond distance in the ZnSe lattice, which is defect trigonal planar as seen in EXAFS, as it would find a minimum energy with Cu in a perfect tetrahedral site. The codopant however, as was previously discussed, is tetrahedral in the ZnSe:Cu,In system and therefore by extension should be also tetrahedral for the other codopants.
The bond distances to its nearest neighbors vary as a consequence of the ion size being different as compared to Zn. As previously mentioned, the D-Se bond distances were: 2.456 Å (Al – Se), 2.481 Å (Ga – Se), and 2.642 Å (In – Se); while the host bond distance was 2.454 Å (Zn – Se).

As was discussed in the EXAFS section, it is possible to place the Cu in a hexagonal site as was indicated in Figure 3.6 (c.). To support the conclusion that Cu is in the distorted tetrahedral site and not in the hexagonal one, the DOS of the hexagonal site is reported in Figure 3.8.

![Figure 3.8](image)

**Figure 3.8**: Density states of Cu in the alternative hexagonal site as indicated in Figure 5 (c.).

With Cu in the hexagonal site, no DOS from the Cu d states were introduced in the bandgap; the d states were seen only within the VB. In this case, Cu could not act as an acceptor and the PL seen in ZnSe:Cu could not be explained. As a result we can rule out this as a possible photoactive dopant site in ZnSe and focus only on the distorted tetrahedral site as the correct structure.
The ion position optimized super cell was then used to calculate the partial density of states (PDOS), the results of which were reported in Figure 3.9. For the host ZnSe system, the predicted $E_g$ was 2.41 eV which is a factor of 0.89x lower than the expected $E_g$ of 2.70 eV. From the PDOS, the VB is primarily Se 2$p$ character hybridized with Zn 4$p$. The CB is a mixture of both Zn 4$p$ and 4$s$ as a result of $sp^3$ hybridization in the tetrahedral ligand field. These states are also well hybridized with Se 2$p$ in the CB.

Doping with both Cu and Al introduces two new states as a result of Cu, these are ligand field split $d$ orbitals forming the $e$ and $t_2$ levels, as well as Al 3$s$ and 3$p$ states. The $e$ orbitals are well hybridized with the VB and reside at the VBM. The $t_2$ orbitals form a separate energy level within the $E_g$ starting at VBM + 0.10 eV and extending to VBM + 0.54 eV. The width of this level, as a consequence of the reduced symmetry of the Cu from the ideal $T_d$, is why the Cu related emission discussed above is broad. The Al related 3$s$ and 3$p$ states are well hybridized with the CB and do not extend below the CBM. The 3$s$ states do contribute to more DOS at the CBM relative to the 3$p$ states, as was also the case for Zn. Consequently the $E_g$ was calculated to be 1.94 eV.

For the Cu only system, the Cu $e$ orbitals are located within the VB and contribute to the VBM while the $t_2$ states are observed between 0.16 and 0.56 eV above the VBM. The defective Zn, adjacent to the V$_{Se}$ and having only bonds to Se, is shown also. The Zn 4$p$ and 4$s$ orbitals have significantly more DOS toward the CBM compared to the bulk Zn but are not seen to extend below the CBM. This is
contrary to our previous report where we observed $V_{\text{Se}}$ states within the $E_g$.[25] These states were removed upon improvements to the computational model by optimizing the local structure around the defect. From the combination of the two results we can conclude that any deviation from the optimum structure will create additional states within the $E_g$ related to the Zn dangling bonds. These states may become activated by phonons or lattice strain. These, and other, effects were not taken into account herein but are likely to play a significant role in the $V_{\text{Se}}$ related emission discussed above and in our previous report. Finally, the calculated $E_g$ was 1.93 eV.

A significant change in the DOS was observed in the ZnSe:Cu,Ga as a consequence of Ga. While the Cu states were the same as previously described ($t_2 = 0.06$ to 0.50 eV above the VBM), a new acceptor state was added at CBM – 0.52 eV related to Ga 4s. Consequently, the resulting $E_g$ was calculated to be 1.56 eV. The remaining Ga 4$p$ states remained well hybridized with the host lattice and mirrored the DOS seen from Zn 4$p$. This result supports the previously discussed model for DAP emission in this system. A similar effect was seen in the ZnSe:Cu,In system however the predicted bandgap is the same as the ZnSe:Cu,Ga system. Seeing that the Cu-Se bond distances were held constant during the optimization procedure for these calculations as DFT could not predict the correct Cu local structure, it can be concluded that the red shift in the PL in ZnSe:Cu,In compared to the ZnSe:Cu,Ga is consequence of a slight change in the Cu local structure between the two codopants.

Shown in Figure 3.10 is the DOS for ZnSe:Cu,Ga in which the Cu-Se bond distances
were not fixed and resulting optimized local structure of Cu became a perfect tetrahedral, as was also the case for Ga. Consequently, the predicted $E_g$ moved to 2.50 eV from 2.56 eV with Cu in the distorted site. This result suggests that in the ZnSe:Cu,In system the Cu local structure is more like the tetrahedral case. From the Cu EXAFS, the ZnSe:Cu,Ga system has increased second and third neighbor peaks.

**Figure 3.9:** Density functional theory calculations of ZnSe:Cu+,D+3 (D = Al, Ga, In, Tl).
and the first neighbor shell is at slightly longer bond distances than the ZnSe:Cu,Al. This result suggests that the Cu in ZnSe:Cu,Ga moves slightly back toward perfect tetrahedral from the more distorted tetrahedra observed in ZnSe:Cu,Al. Likewise, the increased second and third neighbor shells suggest a higher degree of symmetry in the ZnSe:Cu,Ga. Conversely, the ZnSe:Cu,In Cu EXAFS shows decreased second and third neighbor peaks indicating a slightly more disordered environment of the Cu as a result of the increased size of In compared to Ga which more closely matches the host lattice ionic radii. Therefore, while the D^{+3} band in the Ga and In DOS appear the same in these calculations, the increased disorder in the Cu local structure and a

**Figure 3.10** Density of states of ZnSe:Cu,Ga in which both Cu and Ga are in perfect tetrahedral sites (a.). Included as comparison is the DOS with Cu in the distorted tetrahedral site as expected from the EXAFS analysis (b.).
relative shift toward the tetrahedral site can be attributed to the red shift of the PL from Ga to In.

Finally, ZnSe:Cu,Tl was studied as a potential candidate for red emission in this system although it was not synthesized herein. While attempts were made to produce this system synthetically, the large size of Tl is particularly challenging to incorporate and would contribute to significant distortion to the host lattice. The PDOS related to Cu remained the same as previously described however the donor state from Tl 6s moved to CBM – 1.2 eV and extended up to CBM – 0.84 eV. The resulting $E_g$ in this system is calculated to be 0.91 eV. Considering a linear scaling between 1.2 and 1.4 between calculated and experimental, the resulting emission is expected in this system to fall between 1.3 and 1.1 eV, or 950 nm and 1,100 nm. For VBM $\leftarrow$ Tl 4s emission, the calculated transition would be at 1.4 eV; scaled to 1.96 or 1.68 eV, this would represent emission between 630 – 740 nm.

From the results presented herein, it is both experimentally confirmed and theoretically possible to extend ZnSe emission, controllably, from the blue to the red with a combination of doping and codoping strategies. While the Cu related emission in these systems is significantly more broad than the current state of the art CdSe quantum dot systems, the added advantages of minimum self absorption, longer excited state life time, and eliminating Cd in some applications and waste streams is highly desirable.
3.4.4 Improved PL Yield with Custom Designed Capping Ligand

The optical properties of ZnSe quantum dots, and quantum dots in general for that matter, are strongly dictated by the surface. Surface dangling bonds contribute trap states which can severely impact the photoluminescence (PL) quantum yield (QY). Efforts to reduce dangling bond defects have led to improved organic capping ligands as well as inorganic insulating shells. The advantage to the latter approach is the inorganic shell can passivate a greater number of defects compared to organic ligands as organic ligands cannot pack close enough to saturate the dangling bond states on the surface. In addition, inorganic shells are generally considered more robust. For the inorganic shells to be truly effective, both e⁻ and h⁺ should be confined to the fluorescent core so that they cannot access the surface of the QD. It is important to take into account Fermi level alignment when designing core shell systems as after alignment it may still be possible for the photoelectron to enter the shell, as has been suggested previously.[43] For ZnSe, especially, a concentrated approach to managing surface defects is critical as even the most careful and light cleaning techniques post synthesis can be enough to quench the PL.

Herein, we have approached surface passivation with a two pronged methodology. The first was to shell the ZnSe:Cu,D QD core with a ZnS layer. From the vacuum level energetics of the VB and CB, ZnS will insulate both the e⁻ and the h⁺ and keep them confined to the ZnSe core. Once Fermi level alignment is taken into account, however, it is found that the h⁺ is effectively confined but the e⁻ may access the shell however. The second measure taken to complete electronic surface
passivation was with a bidentate thiol based ligand, synthesized by modifying lipoic acid. Lipoic acid is more often used in aqueous synthesis methods or to exchange hydrophobic ligands to improve water solubility.

As water solubility is not desired herein, the acidic functional group of the lipoic acid ligand was used to attach oleylamine making a hydrophobic backbone. This approach was also considered to improve intermolecular ligand stabilization through backbone hydrogen bonding to neighboring ligands through the amide bond.

The synthesis of the modified lipoic acid was shown in Scheme 3.1. A mixture of lipoic acid, oleylamine, and trioctylphosphine were heated to 120 °C for up to 6 hours where a color change from yellow to clear was observed, which was attributed to cleavage of the disulfide bond. During the reaction between lipoic acid and oleylamine, H₂O is released which can react with the trioctylphosphine causing it to become oxidized thus providing electrons to cleave the disulfide bond. The resulting reaction mixture is added directly to the crude ZnSe:Cu,D/ZnS pot where the thiol termination of the ligand offers a strong bidentate interaction with the QD surface at both Zn and S terminations.

Scheme 3.1. Reaction mechanism for the synthesis of the custom capping ligand
The PL of the QDs through the progress of the synthesis was compared in Figure 3.11. The samples were prepared at the same optical density at the excitation wavelength used which was 380 nm (3.26 eV). Prior to the shell addition, both ZnSe:Cu,Al (Figure 3.11, a) and ZnSe:Cu,Ga (Figure 3.11, b) have relatively low PL and the emission could be barely seen with the naked eye. After the ZnS shell was added, the PL was seen to improve in both cases. In ZnSe:Cu,Al the blue portion of the emission was enhanced the most whereas in ZnSe:Cu,Ga the emission related DAP recombination was enhanced. The greatest effect was observed after the custom capping ligand was added however. Post ligand addition, the PL intensity was greatly enhanced, by a factor of 10x at the $\lambda_{max}$, over the entire wavelength range studied. This effect suggests that the ZnS shell was not an ideal insulator for the ZnSe core when considering the photoelectron. After capping ligand addition, Zn dangling bonds at the ZnS surface were fully passivated resulting in a dramatic improvement in the PL yield. The PL was stable after cleaning with a variety of solvent, crashing, and dispersion in DCM with mild heating. This result marks a significant achievement in ZnSe and opens the possibility of using these QDs in real world applications. For long term storage, the QDs dispersed in DCM were stored in a freezer and the PL has been stable for a year at the time of this writing.
3.4.5 Increased Stability of Photocarriers with Codoping Leads to Improved PL Yield

The time dependence of the PL was studied with TCSPC for all the samples discussed above. Using a monochromator before the APD, the $\lambda_{max}$ of the PL peak was recorded as a function of time out to 1,800 ns for the Cu doped samples and to 150 ns for the undoped ZnSe/ZnS sample. The instrument response function (IRF) was 50 ps. These data are presented in Figure 3.12. The ZnSe/ZnS sample decayed much faster than any of the Cu doped samples which persisted for many hundreds of ns. Some differences were observed between Cu,D samples, however clear trends were not apparent. A multi-exponential fitting procedure was applied to each trace using Equation 3.2 in which $\tau_i$ and $A_i$ are the fundamental time constant and the initial amplitude of the $i^{th}$ recombination channel. All the samples studied required a triple exponential fit.

$$I(t) = \sum_{i=1}^{3} A_i e^{-t/\tau_i}$$  \hspace{1cm} (3.2)
From the fit results, the relative photon flux, $\Phi_i$, was calculated by Equation 3.3 which signifies the relative number of photons emitted by the $i^{th}$ process. In general, $\Phi_i$ is much more relevant and informative than $A_i$ when discussing fluorescent processes; and, can be even more informative than $\tau_i$ in some cases.

$$\Phi_i = \frac{\int A_i e^{-t/\tau_i} dt}{\sum_{i=1}^{\beta} \int A_i e^{-t/\tau_i} dt} \times 100\%$$  \hspace{1cm} (3.3)

The fit results for all five samples were presented in Table 3.2 in which $A_i$, $\Phi_i$, and $\tau_i$ are provided, the latter two parameters are shown graphically in Figure 3.13 for the Cu doped samples only. For ZnSe/ZnS (referred to as ‘ZnSe’ in the table), the lifetimes were found to be 0.93, 9.3, and 30 ns which have been related to surface trapping, VBM $\leftarrow$ CBM recombination, and trap state/defect recombination, respectively. The wavelength dependence of these lifetimes are discussed below. The $\Phi_i$ from these transitions were 2.19 % $\pm$ 0.28, 45.1 % $\pm$ 10.4, and 53.9 % $\pm$ 4.5.

Figure 3.12: Time resolved photoluminescence of ZnSe (dark blue), ZnSe:Cu,Al (light blue), ZnSe:Cu (green), ZnSe:Cu,Ga (yellow), and ZnSe:Cu,In (orange). Fit traces are shown superimposed. The time constants used for the fitting are displayed.
The indication is that a majority of the fluorescence process occurs either through VBM ← CBM or trap state/defect level recombination, which is consistent with the expectations from the fluorescence spectrum. From the Gaussian fitting of the PL spectra presented above, the relative peak areas related to either VBM ← CBM or trap state emission was 48.7 and 51.3 %, respectively. These results are consistent the Φ_i obtained by exponential fitting of the time dependent traces. These results also support the proposed kinetic assignments.

In all four Cu doped samples three components were required to obtain an acceptable fit and were on the order of: fast (~10 ns), medium (~100 ns), and long (~600 ns). The fast component was the same, within the fitting error, for three Cu doped samples with the exception of the ZnSe:Cu,Ga/ZnS (‘Cu,Ga’). This sample had a 16 ± 2.5 ns lifetime which was significantly longer than the other samples, i.e. ZnSe:Cu,Al/ZnS (‘Cu,Al’) was 7.5 ± 1.1 ns. The medium lifetime in the Cu samples increased from Cu < Cu,Al ≈ Cu,In < Cu,Ga which were: 87 ns ± 13, 110 ns ± 16, 120 ns ± 18, and 156 ns ± 23; respectively. Finally, the longest time constant, and the most interesting component, increased from Cu = Cu,Al < Ga < In and were found to be: 466 ns ± 70, 476 ns ± 71, 714 ns ± 110, and 825 ns ± 120; respectively. These trends are more easily seen in Figure 3.13. The Φ_i of these components (fast, medium, or long) were similar between the four samples. For the medium component, the Φ_i was essentially the same between Cu and Cu,Al but decreased slightly moving to Cu,Ga and Cu,In. Conversely, the long component, while remaining constant between Cu and Cu,Al, increased slightly for Cu,Ga and Cu,In.
Table 3.2: Triple exponential fitting results of the single wavelength traces from the TCSPC measurements. Wavelengths selected are at the $\lambda_{\text{max}}$. Values and (errors) are reported for the initial amplitude, relative photon flux, and lifetimes /ns. Sample IDs describe: ZnSe/ZnS(ZnSe), ZnSe:Cu,Al/ZnS (Cu,Al), ZnSe:Cu/ZnS (Cu), ZnSe:Cu,Ga/ZnS (Cu,Ga), and ZnSe:Cu:In/ZnS (Cu,In).

<table>
<thead>
<tr>
<th></th>
<th>Amplitude</th>
<th>% Photon Flux</th>
<th>Lifetime /ns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.260 (0.006)</td>
<td>0.535 (0.002)</td>
<td>0.204 (0.054)</td>
</tr>
<tr>
<td>Cu,Al</td>
<td>0.409 (0.005)</td>
<td>0.360 (0.018)</td>
<td>0.231 (0.042)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.494 (0.005)</td>
<td>0.335 (0.019)</td>
<td>0.175 (0.034)</td>
</tr>
<tr>
<td>Cu,Ga</td>
<td>0.408 (0.003)</td>
<td>0.343 (0.016)</td>
<td>0.275 (0.060)</td>
</tr>
<tr>
<td>Cu,In</td>
<td>0.634 (0.003)</td>
<td>0.237 (0.017)</td>
<td>0.131 (0.021)</td>
</tr>
</tbody>
</table>

Figure 3.13: Lifetimes and photon flux of the Cu doped samples: ZnSe:Cu/ZnS (Cu), ZnSe:Cu,Al/ZnS (Cu,Al), ZnSe:Cu,Ga/ZnS (Cu,Ga), and ZnSe:Cu,In (Cu,In). Lifetimes are reported on the left axis and are represented by colored circle markers relating to the fast (green), medium (blue), and long (red) lifetimes. The photon flux are reported on the right axis and are shown as solid gray shaded traces related to the fast (light), medium (darker), and slow (darkest) components. Error bars are also indicated as determined from the triple exponential fitting.

As was discussed previously, the red shift of the PL in Cu,Ga and Cu,In was related to an additional donor level which was introduced into the $E_g$ from the donor $s$ orbitals. The fluorescence process in these materials follows an initial excitation
from a photon from VB to CB. The photoexcited electron and hole are localized/trapped to either the donor state or the Cu d \( t_2 \) band. Cu, being a +1 cation, initially, becomes +2 forming a stable \( d^9 \) configuration. The donor, initially a +3 cation, also becomes +2 upon localization of the photoelectron. The resulting DAP recombination is responsible for the photoemission seen in the Cu,Ga and Cu,In samples and is related to the long time constant. As a result, the added stability of both photocarriers increases the lifetime of the long time constant compared to the Cu and Cu,Al systems, which do not have a significant donor state contribution to the \( E_g \).

It also explains the increase in the \( \Phi_l \) related to this component compared again to the Cu and Cu,Al samples. Carrier localization and stabilization at a DAP center is expected to improve the related recombination channel.

With regard to the Cu and Cu,Al samples, the lifetime and \( \Phi_l \) being essentially equal for the medium and long components, in conjunction with the negligible shift in the PL emission suggests the Al does not play an active role in localizing the photoelectron. The photohole however in these two samples gains increased stability at the Cu\(^+\) site which explains the increased lifetime of the PL process in this system compared to the host ZnSe. Therefore, the long component in these samples is attributed to Cu \( \leftarrow \) CBM recombination.

To discuss the fast and medium components, we turn to the wavelength dependence of the \( \Phi_l \), obtained through singular value decomposition (SVD) global fitting. In this procedure, orthogonal basis vectors are obtained from the convoluted wavelength, time, and intensity dependent spectrum which depend only on
wavelength and time with the intensity component represented in a diagonalized eigenvalue matrix. The time dependent vectors can be fit again using \textbf{Equation 3.2} to obtain time constants free of any wavelength dependence. Likewise, the wavelength dependence of the initial amplitude can also be obtained free of any time dependence. Following this analysis, the $\Phi(\lambda)$ is calculated which has been reported in \textbf{Figure 3.14} for ZnSe, Cu,Al, and Cu,Ga whereas, the remaining samples are presented in the \textbf{Figure 3.15}.

The ZnSe sample was seen to have two distinct peaks related to the 9.3 and 30 ns components. The 9.3 and 30 ns peaks had a $\lambda_{max}$ of 434.2 nm (2.86 eV) and 439.5 nm (2.82 eV), respectively. The peak positions here confirm our previous assertion that the 9.3 ns component is due to $\text{VBM} \leftarrow \text{CBM}$ emission while the 30 ns component is due to trap state emission from a state $E_g - 34$ meV.

With respect to the Cu,Al sample, global fitting resolved an additional component which single wavelength fitting at the $\lambda_{max}$ had missed. The lifetimes obtained from this procedure were 5.5, 21.5, 110, and 476 ns. The relative amplitude of the 5.5 and 21.5 ns components at the $\lambda_{max}$ are quite low compared to the Cu related emission which is why
the additional component was not captured. Both the 5.5 and 21.5 ns peaks were observed in the Cu,Al sample and their relative amplitudes at longer wavelengths were quite low, relatively. The 110 and 476 ns peaks dominated at longer wavelengths but the 476 ns peak contributed significantly more amplitude overall. Because the photoelectron does not have a stabilizing donor state to decay into, competitive processes such as VBM $\rightarrow$ CBM and trap emission can effectively diminish the desirable Cu $\rightarrow$ CBM process. Controllable Cu doping in the system is particularly challenging but would be of specific interest for additional studies where

Figure 3.14: Wavelength dependence of the photon flux for the kinetic components of the fluorescence decay listed for a) ZnSe/ZnS, b) ZnSe:Cu,Al/ZnS, and c) ZnSe:Cu,Ga/ZnS as obtained from SVD-global fitting.
these branching pathways could be more effectively probed. Because the 110 ns process is also clearly centered at the Cu emission, this process may be related to defect Cu, for instance surface doped or $V_{\text{Se}}$ and/or O coordinated.

**Figure 3.15:** Singular value decomposition global fitting results of the normalized photon flux as a function of wavelength for ZnSe:Cu/ZnS (a.) and ZnSe:Cu,In/ZnS (b.)

In the Cu,Ga case, the 5 - 10 ns component was not observed in the data indicating that the Ga donor state is an effective and efficient trap of photoelectrons. DAP emission, 714 ns, centered at 548 nm (2.26 eV) clearly dominates in this sample as the 156 ns peak, centered at 545 nm (2.27 eV) is relatively much weaker compared to the Cu,Al sample. Because Ga$^{+3}$ is very nearly the same size and is isoelectronic with Zn$^{+2}$, more effective incorporation of Ga into the host lattice is expected compared to Al or In. As a result, Cu$^+$ can be more easily incorporated into the host
lattice having a stable and effective counter ion to balance the charge imbalance created upon replacing Zn\(^{+2}\) with Cu\(^{+}\). Improved doping quality in the Cu, Ga sample explains the large increase in the 714 ns peak relative to the 156 ns peak. The relative photon flux, calculated by integrating the Gaussian fit peaks shown in Figure 3.14 c, was similar to those obtained from single wavelength fitting: 3, 19, and 78 % for the fast, medium, and slow components, respectively.

Finally, the In doped system exhibits increased strain due to the large In size which consequently reduced doping quality. The resulting $\Phi_i$ of the DAP channel decreased relative to increased recombination from the competitive processes from the host lattice.

### 3.5 Conclusions

A series of Cu\(^{+}\) doped ZnSe NCs with the incorporation of a trivalent codopants (Al\(^{+3}\), Ga\(^{+3}\), or In\(^{+3}\)) were prepared which demonstrated tunable fluorescence from green to orange. To improve the PL yield and long term stability, a ZnS shell was incorporated to passivate surface dangling bonds and insulate photogenerated carriers but marked enhancement was not obvious. A 10x increase in PL intensity was achieved however through the use of a custom capping ligand synthesized herein. This approach was effective for undoped ZnSe as well and added solvent stability to the PL which had not been seen previously by us. A series of samples: ZnSe/ZnS, ZnSe:Cu/ZnS, ZnSe:Cu,Al/ZnS, ZnSe:Cu,Ga/ZnS, and ZnSe:Cu,Ga/ZnS were characterized by a number of methods to understand the PL processes and the origin of the redshift in the PL with the addition of Ga and In.
EXAFS confirmed that Cu occupies a distorted tetrahedral site in the lattice while the codopants have a tetrahedral geometry, both of which are added to the lattice by substituting Zn. The disorder in the local structure around the dopant decreased with the addition of co-dopants. Computational studies on a model system with DFT show a hole acceptor state which is introduced by Cu $t_2$ orbitals. Both Ga and In added electron acceptor states into the bandgap below the CB. The codopants had the role of charge compensation of the lattice for the Cu doping which improved Cu incorporation as a $V_{\text{Se}}$ is not required, as is the case in the ZnSe:Cu system. Time resolved photoluminescence studies revealed that Cu doping helps to stabilize the photohole while the addition of Ga and In can stabilize the photoelectron. The combined effect is fluorescence lifetimes extending out to 825. An electronic structure picture was developed to explain the location of donor and acceptor levels in these systems. In all, a combined approached used here to improve PL quantum yield by effective surface passivation and stabilizing photogenerated carriers is demonstrated. In addition, the tunable PL in ZnSe from blue to orange with added long term stability offers an exciting alternative to CdSe based fluorophores for next generation LED technologies.

3.6 References


CHAPTER 4: Simultaneous Detection of Two-element Kβ XES Spectra

Using Energy Dispersive Spectrometer

4.1 Abstract

The multielectron catalytic reactions, such as water oxidation, nitrogen reduction, or hydrogen production in natural enzymes and inorganic catalysts, often involves multimetallic clusters, where the reaction is controlled by the electronic and spin coupling between metals and ligands to facilitate charge transfer, bond formation/breaking, substrate binding, and release of products. In this study, we present a method to detect X-ray emission signal from multiple elements simultaneously, and study the changes in electron structure and sequential chemistry that occurs between elements. Kβ X-ray emission spectra (XES) probe charge and spin states of metals as well as their ligand environment, critical for understanding the functional role of redox-active metal sites. A wavelength dispersive spectrometer based on the von-Hamos geometry was used, that disperses Kβ signals of multiple elements into an area detector, and enables an XES spectrum to be measured in a single-shot mode. This overcomes the scanning needs of the Rowland circle spectrometers, and the data is free from temporal and normalization errors, and therefore ideal to follow sequential chemistry at multiple sites.

In this study, we applied this method to MnOx electrocatalysts, and investigated the effect of secondary element Ni in the catalytic activity. Electro-deposited Mn oxide catalyses oxygen-evolution reaction (OER) and oxygen-reduction reaction (ORR) at different electrochemical potentials under alkaline condition.
Incorporation of Ni was found to reduce the low valent Mn component resulting in higher average oxidation state of Mn in MnNiOx under ORR and OER conditions, when compared to MnOx under the same conditions. The reversibility of the electrocatalyst was also improved by the presence of Ni. The detection of the XES signal from both Ni and Mn sites allows correlating the changes at two metal sites during the electrochemistry. The detection scheme we described here can be applicable to the time-resolved multi-element study to follow the dynamics of catalytic and electron transfer reactions.

4.2 Introduction

Many of the inorganic catalysts and natural enzymes involve multi-electrons, and require several steps to complete reactions. In natural systems, the rate and the directionality of the electron-flow are well-controlled by the spatially and temporally separated moiety at various levels, within molecules (e.g. MnFe ribonucleotide reductase), between pigments (e.g. cytochrome c oxidase), or between one system and another (e.g. between P and FeMo cluster in nitrogenase). Such systems often consist of multiple transition metals that go through several redox states during the reaction. Similarly, controlling electron flow between multiple sites is a key issue for developing materials such as artificial photosynthetic devices and magnetic materials. In this paper, we present a detection scheme of X-ray emission signals to simultaneously follow the chemistry at multiple sites by probing the element/orbital/spin-specific signals, in order to understand dynamics of catalysis and electron transfer reactions.
X-ray emission spectroscopy (XES) has proven to be a powerful technique in the past few years when used with high brilliance X-ray photons that modern synchrotron radiation sources offer. Complementary to X-ray absorption spectroscopy (XAS), XES probes the occupied electronic orbitals of 3$d$ transition metals by measuring emitted photons from orbitals at higher energy into a 1$s$ ($K$-edge) hole after the excitation event. Each emission peak is characteristic of the orbital that the electron is emitted from, and contains unique chemical information such as charge/spin state information, ligand properties, and symmetry.[1] Among the various X-ray emission lines, $K\beta_{1,3}$ and $K\beta'$ transitions correspond to metal 3$p$ to 1$s$ decay, and its peak position reflects the number of unpaired electrons through the 3$p$/3$d$ exchange interaction. Therefore, the spectra are sensitive to the oxidation state and spin state of metal site. XES has also been recently used to provide local geometric/electronic structures of an element of interest in the field of metalloenzymes and inorganic catalysts.[2, 3]

Among the several X-ray spectroscopy techniques, XES is capable of simultaneously probing multiple metal sites in the sample. As shown in Scheme 1, a single incident X-ray energy can excite metals when it is above their electron binding energy without scanning the monochromator for incoming X-rays. The use of an energy dispersive spectrometer combined with a position sensitive detector further eliminates the requirement to scan the photons-out spectrum (i.e. analyzer crystals and detector), unlike commonly used spectrometers based on the Rowland circle geometry. Recently, we have developed a multi-crystal von-Hamos type
spectrometer that is designed for shot-to-shot collection of transition metal $K$-edge emission spectra.\cite{4} The spectrometer has been used to take shot-by-shot measurements at an X-ray free electron laser facility, enabling the use of XES simultaneously with other techniques such as X-ray Diffraction (XRD) or scattering measurements. In the current study, we used this energy dispersive spectrometer to probe multiple metal sites simultaneously by different crystal reflections that disperse the emission signal from each metal onto a separate line on the 2D detector. This detection scheme simplifies a comparison of the changes in different element sites, by circumventing systematic errors often induced by the concentration and volume distribution of the sample, normalization, timing errors when measurements were conducted independently.

### Scheme 1: $K\beta$ energy diagram with two elements being excited simultaneously.
As an example, we have studied Mn oxide along with the Mn and Ni mixed oxide electrocatalysts that can bifunctionally catalyse the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Development of catalytic materials that can convert between O₂ and H₂O is important in renewable energy technologies, including fuel cells, metal-air batteries, electrolysis cells, and solar fuel synthesis. A bifunctional catalyst is important to a device that combines artificial photosynthesis process with a fuel cell. OER is the anode reaction in artificial photosynthesis/water oxidation, while ORR is the cathode reaction in fuel cells. Having bifunctional catalysts that can serve for both ORR and OER in high activity is one of the major challenges in energy conversion and storage technologies, and it is necessary to improve understanding of the chemical state under reaction conditions.

Recently, we performed in-situ XAS measurements on a bifunctional manganese oxide (MnOₓ) catalyst with high electrochemical activity for both ORR and OER. From the XANES and EXAFS study on the Mn bifunctional catalysts deposited on a gold-coated silicon nitride (Au-Si₃N₄) window, we found that the switch from ORR to OER potentials results in a structural change in MnOₓ/Au-Si₃N₄ catalyst and identified MnO₅ phases relevant to each set of conditions; under ORR condition, the MnOx is primarily in disordered Mn₃O₄ form, while under OER condition, it becomes birnessite-like structure. Recently, there has been an active investigation of the effect of additional metals in the system that modulates the catalytic performance of those oxide-based electrocatalysts.[5] In the current study,
we investigate the effect of Ni in the MnOx OER and ORR bifunctional electrocatalyst with XES using wavelength-dispersive spectrometer.

4.3 Experimental Section

4.3.1 Model Compounds

NaNiO$_2$ was synthesized by annealing Na$_2$O$_2$ and NiO in a stream of O$_2$ as reported previously.[6] NaNiO$_2$ was used to prepare γ-NiOOH by treating it with 5 mol equivalent of Br$_2$ in acetonitrile.[6] For β-NiOOH a suspension of Ni(OH)$_2$ in 3 M aqueous KOH was treated with 0.7 mol equivalents of Br$_2$. NiO, Na$_2$O$_2$, Ni(OH)$_2$, KOH, Br$_2$, and K$_2$Ni(H$_2$IO$_6$)$_2$ were purchased from Aldrich.

Mn$_3^{II,III,III}$O$_4$ was purchased from Sigma-Aldrich. The details of synthesis and characterization of β-Mn$_4^{IV}$O$_2$ and α-Mn$_2$O$_3$ are described in previous study,[7] whereas description of Mg$^{2+}$ birnessite is reported in the work published by Web et al.[8]

4.3.2 Electrodeposition of Oxide Catalysts

Prior to manganese oxide (MnO$_x$) electrodeposition, silicon nitride membrane (Si$_3$N$_4$) windows (1000 nm membrane, Silson Ltd.) were sputter coated with a 10 nm binding layer of titanium and a 100 nm layer of gold to establish conductive substrate (Au-Si$_3$N$_4$). Electrodeposition was carried out in a N$_2$-purged three electrode electrochemical cell with the Au-Si$_3$N$_4$ membrane window as the working electrode, a graphite rod as the counter electrode, and an Ag/AgCl reference electrode. The deposition was performed by adopting a known literature procedure[9, 10] in a solution consisting of 0.71 g of sodium sulfate (Sigma-Aldrich, >99.0%) and 1.23 g
of manganous acetate (Aldrich, 99.99%) dissolved in 50 mL of Millipore water at room temperature, yielding a solution with pH of 7.4. The solution was then aged for 6 days, until the pH dropped to approximately 7. Before performing electrodeposition, the resistance between the working and reference electrodes was measured to ensure proper electrical contact between copper tape and the gold layer of Au-Si$_3$N$_4$. After establishing a proper contact and achieving a resistance of 30-60 Ω, the potential was iR compensated to 85% and cycled nine times between 0.0 and 0.6 V vs Ag|AgCl at a sweep rate of 20 mV·s$^{-1}$. For MnNiOx sample the electrodeposition electrolyte was prepared by dissolving 0.551 g of manganous acetate (Aldrich, 99.99%), 0.560 g of nickel(II) acetate (Aldrich, 99.998%), and 0.639 g of sodium sulfate (Sigma-Aldrich, > 99.0%) in 45 mL of Millipore water. In a typical electrodeposition cycle, the potential was held at 0.57 V to pass 2.5 mC of charge for Mn deposition before switching the potential to -0.88 V to pass 2.5 mC of charge for Ni deposition. The system was then rested for 5 seconds before repeating the deposition again for a total of 20 cycles. The entire deposition process took roughly 5 minutes to complete.

4.3.3 Physical Characterization

Scanning electron microscopy (SEM, FEI Magellan 400 XHR) was used to determine the thickness of NiMnO$_x$ on Au-Si$_3$N$_4$. Prior to SEM characterization, the membrane window was shattered and a shard of the Au-Si$_3$N$_4$ window was imaged. Shattering was necessary since the Au-Si$_3$N$_4$ window is surrounded by a supporting frame and electrodeposition typically results in more material deposition at the edges than in the middle. Imaging the unbroken membrane window would have resulted in
an overestimation of the actual catalyst thickness on the Au-Si$_3$N$_4$ window. The sample stage was tilted at a 60 degree angle and a 15 pA beam current of 1 kV and a backscatter electron detector were used. A representative SEM image is shown in Figure 4.1 (a), and sample thickness of 120 nm was estimated. Physical characterization of MnOx sample has been reported in previous work.[7]

4.3.4 Electrochemical Characterization

The oxygen reduction and oxygen evolution activities of the NiMnO$_x$, and MnO$_x$ catalysts were evaluated in a three electrode electrochemical cell with a graphite rod counter electrode, an Ag/AgCl reference electrode, and 0.1 M potassium hydroxide (KOH) electrolyte. The headspace of the cell was purged with O$_2$. Cyclic voltammetry (CV) was carried out at a sweep rate of 20 mV/s in a potential region of 0.35 V to 1.78 V vs. RHE. All scans were 100 % IR-compensated. The potential scale was calibrated to a reversible hydrogen electrode (RHE) using a platinum wire as the working electrode in a hydrogen-saturated electrolyte. The reversible hydrogen potential (0.00 V versus RHE) was taken to be the potential at which the current is zero, and a value of -0.957 V was obtained. The cyclic voltamograms of MnOx and MnNiOx samples have been compared in Figure 4.1 (b), and a considerably improved OER activity is noticeable in case of MnNiOx.
4.3.5 **In situ XES data collection.**

The experiment was performed at beamline 5.0.2 of the Advance Light Source (ALS) synchrotron facility. The incident X-ray beam, focused down to 1 x 2 mm$^2$ (vert x horz), had a flux of ~ $4 \times 10^{12}$ photons/sec and an energy of 10.4 keV. XES spectra were recorded by means of a multi-crystal wavelength dispersive hard X-ray spectrometer based on the Von-Hamos geometry (Figure 4.2). The spectrometer provides high-energy-resolution (~1 eV) and a large solid angle collection (1.3 % of the sphere). An array of up to 4x4 crystal analyzers diffracts and focuses the emitted radiation from the sample to a 2-D detector following Bragg’s law, $n\lambda = 2dsin\theta$. The crystal analyzers, which are 110 x 25 mm$^2$ (horizontal x vertical), are cylindrically bent with a radius of curvature of 500 mm perpendicular to the scattering plane. For each crystal analyzer, integration along the focusing direction of the signal on the
detector results in an emission spectrum. This setup enables an XES spectrum to be measured in a dispersive mode, overcoming the scanning needs of the Rowland circle spectrometers. [4] The angle between the incident and emitted X-rays (scattering angle) was set to 90 degrees to minimize the contribution of the unwanted elastic scattering from the sample.

A subset of 12 Si(440) crystals was used to collect the signal from the Mn Kβ region 6472 eV to 6498 eV, and focus it in one line on a Pilatus 100k detector. Simultaneously, a second Pilatus 100k detector was used to record the Ni Kβ signal (8235 eV to 8300 eV) from a second subset of 4 Si(551). All the spectra were normalized to the incident flux $I_0$ measured with a gas filled ion chamber and cross-calibrated to the published value of 6490.40 eV for the 1st moment (integrated from 6485 – 6495 eV) of Mn$_2$O$_3$.[11]
4.3.6 XAS Data Collection

The XAS measurements at Mn and Ni K-edges were performed on beamline 7-3 at Stanford Synchrotron Radiation Laboratory (SSRL) with average current of 500 mA at an electron energy of 3.0 GeV. A Si (220) double crystal was used to monochromatize the radiation and then detune the radiation to 50% of flux maximum at Mn/Ni K-edge, thereby attenuating the effects of higher harmonics. Fluctuations in the incident beam intensity were monitored using a N₂-filled chamber (I₀) in front of the sample. XAS spectra were also collected for the reference samples mentioned for
XES and energy was calibrated using the Ni foil/KMnO$_4$ placed between two N$_2$-filled chambers (I$_1$ and I$_2$) after the sample. In case of Ni, the spectra were calibrated with respect to the first peak maximum of first derivative for nickel foil (833.0 eV), whereas the corresponding peak for Mn K-edge of KMnO$_4$ was calibrated to 6543.3 eV. For in-situ measurements, the energy was calibrated using a glitch in the I$_0$. The data was collected at room temperature in fluorescence excitation mode using a 30 element Ge detector (Canberra).

Data analysis was done using the standard programs based on IFEFFIT.[12, 13] The spectra were normalized with respect to the edge height after subtracting the pre-edge and post-edge backgrounds using Athena software. To extract EXAFS oscillations, background was removed in k-space using a five-domain cubic spline. The resulting k-space data, $k^3 \chi(k)$, was then FT to r-space.

**4.3.7 Electrochemical Cell Setup:**

A H-shaped electrochemical cell was used for *in situ* X-ray spectroscopy, in which Si$_3$N$_4$ window was mounted on one surface. The electrochemical cell was positioned at an angle of 45° between the surface of the sample and the incident X-ray beam (Figure 4.2 a). In the setup, the backside of Si$_3$N$_4$ window was exposed to X-rays, while the front side of Si$_3$N$_4$ window with electrodeposited MnO$_x$ on Au/Ti layer faced into the interior of a two-compartment electrochemical cell. Electrochemistry was performed in air using Ag/AgCl reference electrode, platinum wire counter electrode, and 0.1 M KOH electrolyte. Although RHE calibration was not performed during *in-situ* XES/XAS characterization, we assumed the same shift
of 0.960 V for Ag|AgCl reference electrode and report all potentials vs. RHE. After preparing the electrochemical cell for in-situ XES/XAS measurements, the resistance between the working and reference electrodes was measured to ensure proper electrical contact between the potentiostat and MnO$_x$ on Au-Si$_3$N$_4$. After achieving a resistance of 150 $\Omega$, a CV was performed from 0.05 to 1.1 V in air, to record electrochemical features of the working electrode.

For comparison, several Mn oxide powder samples, Mn$^{II}$O, Mn$^{III}_2$O$_3$, Mn$^{IV}$O$_2$, Mn$^{III}$OOH, and Mn minerals like Mn birnessite (Mn$^{III}$/Mn$^{IV}$) and Mn todorokite (Mn$^{III}$/Mn$^{IV}$) were also collected using the same energy-dispersive XES spectrometer. As Ni reference samples, the XES spectra of Ni$^{II}$(OH)$_2$, $\beta$–NiOOH, $\gamma$–NiOOH, NaNiO$_2$, and K$_2$Ni$^{IV}$(H$_2$IO$_6$)$_2$ (potassium nickel(IV) paraperiodate, NiPPI) were collected. The samples of these model compounds were prepared by diluting them with boron nitride (1% w/w) and enclosing the powder in an aluminum holder with Kapton tape windows on both sides.

4.4 Results and Discussion

4.4.1 XES under ORR and OER condition

4.4.1.1 MnO$_x$. 

**Figure 4.3(a)** shows the Mn K$\beta_{1,3}$ and K$\beta'$ emission spectra of ORR and OER catalysts collected at 0.8 V and 1.7 V. The K$\beta_{1,3}$ peak arises from the emission process of Mn 3p to 1s transition, with constructive spin configuration. Accompanying K$\beta'$ peak corresponds to the destructive spin configuration; the mechanism has been illustrated by schematic representation in **Figure 4.3 (a)**.
Together, both peaks reflect the number of unpaired electrons through the 3p/3d spin exchange interactions. There is smaller 3p/3d exchange interaction with the decrease in spin and peaks move towards each other with decreasing spin. In a previous study, we have identified the ORR catalytic phase to be in disordered Mn$_3$O$_4$ like phase, and the OER phase to be a mixed Mn$^{\text{III,IV}}$ oxide having birnessite-like structure.[7]

Upon changing the potential from 0.7 V to 1.8 V, a shift in K$\beta_{1,3}$ peak position to lower energies is quite obvious in Figure 4.3(a), indicating a change to higher oxidation state of Mn. In addition, a variation in the intensity of K$\beta'$ is observed for the two phases involved in catalytic reactions, consistent with the oxidation state changes. Figure 4.3 (b) compares the XES spectrum of ORR phase (0.7 V) with the emission spectra of standard manganese oxide phases with different oxidation states. Though the higher energy side of the K$\beta_{1,3}$ peak for ORR catalyst aligns well with that of Mn$_3$O$_4$, the lower energy part of the main line extends further towards lower energies as compared to that for Mn$_3$O$_4$. This indicates that there is a higher Mn$^{3+}$/Mn$^{2+}$ ratio in ORR phase as compared to that in Mn$_3$O$_4$. When the potential is changed to 1.8 V, corresponding to OER phase, the emission spectrum obtained aligns well with that of birnessite as shown in Figure 4.3 (c), and the peak position appears at a slightly higher energy than that for MnO$_2$. This is a further evidence of results observed in our recent in-situ XANES investigation of this material.[7]
Figure 4.3: (a) $K\beta_{1,3}$ XES spectra at 0.7 V (ORR) and 1.8 V (OER). The inset shows the transition scheme of the $K\beta_{1,3}$ and $K\beta'$ emission process. (b) Comparison of Mn model compounds’ XES spectra to ORR catalyst with the inset having a zoomed in view of the main peak. (c) XES profile of the catalyst held at OER relevant potential compared with the reference Mn compounds.
4.4.1.1 Phase Evolution Between ORR and OER

To study the transitions between the ORR and OER phases and extract information regarding energy storage mechanism during the electrochemical cycle, \textit{in-situ} XES spectra were recorded while stepwise sweeping the potential. Figure 4.4 (a) presents a series of 23 K$\beta_{1,3}$ XES spectra collected under a succession of potentials, starting from 0.7 to 1.8 V vs RHE and then back to 0.7 V with a step size of 0.1 V. The collection time for each spectrum was 15 minutes during which the corresponding potential was held constant. Spectra of Mn$_3$O$_4$ and birnessite are also plotted for comparison. Although there is not much difference in the shape of the spectra, a gradual change in the energy of the peak maximum can be clearly recognized. The peak successively shifts to lower energies with increasing applied potential (red spectra) and then back to higher energies as the potential is decreased stepwise (black spectra). The K$\beta_{1,3}$ peak is normally asymmetric due the final states involving spin-flip excitations accompanying 3p to 1s decay.[1] Instead of comparing the peak tops of asymmetric peaks, a more sensitive way is to compare the centers of gravity of the peaks, also called first moments. To determine the first moments’ values, the spectra were first normalized by area and then 1$^{st}$-moment values were calculated between 6485-6495 eV using eq. 4.1[14]

\[ 1st - Moment = \frac{\Sigma_j E_j l_j}{\Sigma_j l_j} \] (1)

Where \( E_j \) and \( l_j \) denote the energies and intensities of the \( j \)th point, respectively. The 1$^{st}$-moment values have been plotted in Figure 4.4 (b), for forward as well as reverse potential sweep. The shift is related to decrease in the energy
difference between $3p$ and $1s$ levels with increasing oxidation state and vice versa. For forward sweep, the first moment value starts decreasing after 0.9 V signifying the oxidation of metal center. During the backward sweep of potential, the reaction center starts getting reduced after the potential is decreased below 1.5 V. As indicated by the plot, the 1st moment values are not recovering completely indicating that a part of the sample is stuck at higher oxidation state.

**Figure 4.4:** (a) Evolution of the XES $K\beta_{1,3}$ spectrum along the forward (red) and reverse (black) potential changes. Corresponding reference spectra have been plotted for extreme potentials. (b) 1st moment energy changes during forward (blue) and backward (red) sweep of potentials.

4.4.1.2 MnNiO$_x$.

To manifest the feasibility and usefulness of the simultaneously probing two metal centers, MnO$_x$ was doped with Ni. The incorporation of Ni has been reported to improve the reaction kinetics and electrochemical stability of the catalyst.[15, 16]
Mn and Ni Kβ1,3 were collected simultaneously at different potentials along the CV curve between 0.4 V to 1.8 V, with a step size of 0.2 V. Representative spectra at different potentials are shown in **Figure 4.5 (a)** and **(c)** for Mn and Ni, respectively. Again, a considerable shift in the peak maximum is observed for Mn Kβ1,3 as the potential is moved from ORR to OER conditions. To make the changes look more prominent, 1st moment energy values obtained using eq. 1 and calculated between 6485-6495 eV, have been plotted in **Figure 4.5 (b)**, along with the comparison with MnOx sample as an inset. The first moment energy position corresponding to ORR is slightly smaller than that of MnOx sample, suggesting a comparatively higher oxidation state of Mn. Ni doping has been reported to decrease the lower oxidation state Mn content.[16] In addition, the oxidation state increases more sharply between ORR and OER as indicated by the slope of 1st moment curve between 0.8-1.2 V, suggesting that Ni is improving the kinetics of the reaction. The 1st moment energy position of OER phase is ~6490 eV which very close to the one observed for MnO2.[1] Therefore, we expect the oxidation state of Mn close to +4 under OER conditions. While the phase was not recovering completely during the reverse potential sweep in case of MnOx (figure 4.4), it recovers considerably well in case of MnNiOx as indicated by the spectra in **Figure 4.5 (a)** and 1st moment values in **Figure 4.5 (b)**.
Figure 4.5: (a) Mn Kβ₁,₃ X-ray emission spectra from a 1:1 mixture of Mn/Ni electrocatalyst measured simultaneously with Ni using the setup illustrated in Fig. 2 with 100 seconds integration time under different potential. (b) 1st moment energy change of Mn spectra measure under different potentials. (c) Kβ₁,₃ of Ni measured with increasing potential along with Mn. (d) Change in the first moment energy position in Ni spectra during the step-wise increase of potential.

The Ni Kβ₁,₃ spectra are represented in Figure 4.5 (c) along with the corresponding 1st moment values in Figure 4.5 (d). The spectral shift is quite small between ORR and OER phases, but it can be clearly seen looking the 1st moment
The biggest change is observed between 1.2 and 1.4 V, which is consistent with the oxidation of Ni as observed in CV curve (Figure 4.1 b). To examine the change more closely, the spectra of ORR and OER phases have been overlaid in Figure 4.6 (a). The difference is quite obvious on the high energy side of the spectrum where the ORR spectrum extends to slightly higher energies as compared to OER. In Figure 4.6 (b) the spectra under reduction and oxidation conditions have been plotted together with the reference compounds having Ni in different oxidation states. The peak appears at higher energy for Ni(OH)$_2$ which has the smallest oxidation state of Ni, therefore, largest energy difference between $3p$ and $1s$. The peak for ORR phase is at lower energy as compared to that of Ni(OH)$_2$, the difference being more evident on the high energy side. The XES spectrum of β-NiOOH lies close to ORR, suggesting that Ni in ORR phase would have an oxidation state slightly less than +3, as the ORR spectrum on the right side extends beyond that of β-NiOOH. Emission trace for OER phase resembles with γ-NiOOH as the spectrum of β-NiOOH encompasses it on both sides. Based on the in situ XAS studies Ni based films, γ-NiOOH has been recognized previously as the active catalyst for water oxidation.[17, 18] It has a layered structure with large interlayer distance, and Na$^+$/K$^+$ ions within the layers along with water.[19] Overcharging of β-NiOOH in the presence of K$^+$ and water produces a common form of γ-NiOOH denoted by H$_x$K$_{0.33}$(H$_2$O)$_{0.66}$NiO$_2$.[19, 20]
Figure 4.6: (a) Ni Kβ1,3 XES spectra of the electrocatalyst under ORR (red) and OER (green) conditions. (b) Spectra of ORR and OER phases overlaid with those of reference compounds with different formal oxidation states of Ni.
4.4.2 *In Situ* XANES

4.4.2.1 Nickel K-edge.

To further complement the XES results, *in situ* XAS spectra were measured while exposing the sample to ORR and OER relevant potentials of 0.7 V and 1.8 V, respectively. Ni K-edge spectra corresponding to as-prepared, ORR and OER phase are represented in Figure 4.7 (a). Although XANES features are almost similar for as-prepared and ORR phase, the edge position, as measured at half height position of the edge jump (intensity value 0.5), shifts to higher energy by 0.2 eV (8343.2 eV for as-prepared and 8343.4 eV for ORR phase) indicating a slight increase in the overall oxidation state of Ni under ORR conditions. Increasing the potential to 1.8 V, corresponding to the OER phase, results in shifting the edge position to 8345.8 eV representing a shift of 2.4 eV as compared to ORR phase. In Figure 4.7 (b) XANES spectrum of the ORR phase is compared with the model compounds Ni(OH)$_2$, NaNiO$_2$, β-NiOOH and γ-NiOOH, carrying formal Ni oxidation states of +2, +3, +3 and 3.6, respectively. The half-edge position of ORR phase (8343.4 eV) appears at ~1.0 eV higher energy than Ni(OH)$_2$ (8342.7 eV) and is very close to β-NiOOH (8343.9 eV) and NaNiO$_2$, indicating a Ni oxidation state slightly less than +3. This suggests that ORR phase could be a mixture of phases and further discussion is followed based on EXAFS results. The area under the first peak, which is also called white line (WL), corresponds to the unoccupied density of states. The WL intensity is larger for the sample as compared to the reference compounds with comparable oxidation states. This might result from the stronger hybridization between oxygen
and nickel in MnNiOx sample in comparison to the model compounds as the oxygen atoms would be shared between Ni and Mn. Stronger hybridization between Ni-O is expected as Ni is more electronegative (electronegativity 1.9) than Mn (electronegativity 1.6), and therefore, electronegativity difference is smaller in case of Ni-O leading to increased covalency of Ni-O bond in MnNiOx. This result suggests that there is no phase separation and Ni and Mn are well mixed into the lattice.

The XANES spectrum of OER phase is compared to β-NiOOH, NaNiO₂, γ-NiOOH and NiPPI in Figure 4.7 (c). Ni in NiPPI is +4 oxidation state and maximum oxidation state of +3.66 has been reported for γ-NiOOH.[6, 19-21] Based on the edge position (8345.8 eV) the sample seemed to have an average oxidation state of Ni very close to that of Ni in γ-NiOOH (8346.1 eV), more reduced than stoichiometric Ni(IV) compound NiPPI with an edge position of 8346.4 eV. Therefore, we expect an average oxidation state between +2.9 and +3.6, that will be further discussed based on EXAFS data.
Figure 4.7: (a) Comparison of Ni K-edge XANES spectra measured for as-prepared MnNiOx sample and after in situ exposure to ORR and OER relevant potentials. (b) Spectrum of MnNiOx sample poised at 0.7 V overlaid with those of Ni(OH)$_2$, $\beta$-NiOOH, NaNiO$_2$ and $\gamma$-NiOOH. (c) MnNiO$_x$ sample under OER conditions compared with $\beta$-NiOOH, NaNiO$_2$, $\gamma$-NiOOH and NiPPI.
4.4.2.2 Manganese K-edge.

Figure 4.8 (a) compares the Mn K-edge X-ray absorption spectra corresponding to dry (ex-situ), ORR and OER phases. It is quite obvious that applying a potential of 0.7 V shifts the rising edge position of the spectrum to higher energy as compared to that of dry sample indicating an increase in oxidation state. Subsequent increase in potential to OER conditions (1.8 V) results in further oxidation of the Mn species as indicated by the shift of edge position to higher energy.

In Figure 4.8 (b) XANES spectrum of ORR phase is compared with the spectra of Mn$_{3}^{II,III,III}$O$_4$, α-Mn$_2^{III}$O$_3$, γ-Mn$^{III}$OOH, β-Mn$^{IV}$O$_2$ and birnessite, which is a naturally occurring Mn mineral with a layered structure having cations (Mn$^{n+}$) and water between the layers. Based on the edge position, ORR phase is more oxidized than Mn$_{3}^{II,III,III}$O$_4$ and α-Mn$_2^{III}$O$_3$, but more reduced than β-MnO$_2$, and resembles closely with birnessite phase, indicating an oxidation state close to 3.7. Synthetic forms of birnessite such as triclinic Mg$^{2+}$-birnessite, whose spectrum is shown in the figure, normally have 20-40% Mn$^{II}$ in Mn$^{IV}$O$_2$,[22-24] leading to an average oxidation state of 3.6-3.8. ORR phase also shows similarities with todorokite phase which can also accommodate cations in the structure, however the presence of birnessite like phase is more likely as it can be formed electrochemically at room temperature,[25, 26] whereas formation of todorokite like phase requires higher temperature or high pressure.[24, 27] Thus, under ORR conditions the catalaytic phase has Mn in an oxidation state close to birnessite, which is higher than in ORR phase without Ni. This is consistent with the XES results under reduction potentials.
Figure 4.8: (a) Mn K-edge XANES spectra of as-prepared MnNiO$_x$ sample compared with the spectra collected in situ under ORR and OER conditions. (b) Spectrum of MnNiO$_x$ film poised at 0.7 V compared with Mn$_3$O$_4$, α-Mn$_2$O$_3$, γ-MnOOH, Mg$^{2+}$-birnessite. (c) MnNiO$_x$ sample held at 1.8 V overlaid with α-Mn$_2$O$_3$, Mg$^{2+}$-birnessite, Todorokite, β-MnO$_2$ and λ-MnO$_2$.
Figure 4.8 (c) shows the Mn K-edge spectrum of MnNiO$_x$/Au-Si$_3$N$_4$ catalyst when poised at OER potential, along with the XAS spectra of $\alpha$-Mn$_2^{III}$O$_3$, birnessite, todorokite, $\beta$-MnO$_2$ and $\lambda$-MnO$_2$. The rising edge position of the OER catalyst appears at higher energy than those of $\alpha$-Mn$_2^{III}$O$_3$, birnessite and todorokite, indicating that the catalytic phase is more oxidized than these reference samples. The edge position of the sample is very close to $\beta$-MnO$_2$ and $\lambda$-MnO$_2$, but the XANES features show strong similarities to later. This reveals that Mn$^{IV}$ content in OER phase is higher than that in birnessite or todorkite, suggesting an oxidation state of $\sim$4.0 for OER catalyst, confirming the XES results.

4.4.3 In Situ EXAFS

4.4.3.1 Nickel.

Further information regarding the evolution of phases during the catalytic processes was obtained by EXAFS. FT of $k^3$-weighted oscillations are presented in Figure 4.9 (a) for ex-situ (dry), ORR and OER phases. The structural motifs corresponding to each peak have also been shown with arrows highlighting the absorber scatterer pairs. It is important to note that the distances indicated by the peak positions are shorter by 0.3-0.4 Å relative to the true distances, due to phase shift.

Spectra for dry and ORR catalyst exhibit marginal differences, with slight increase in the FT amplitude for the first peak that corresponds to first neighbor shell consisting of Ni-O octahedra. This is likely due to the transformation towards the phase with more organized structure since under alkaline conditions $\alpha$-Ni(OH)$_2$.zH$_2$O which has water between the Ni-OH layers, changes to $\beta$-Ni(OH)$_2$. Also a slight
oxidation was observed in XANES which might result in small fraction of Ni$^{3+}$ in the form of β-NiOOH like structure. Increasing the potential to 1.8 V, relevant to OER, results in shifting the peak positions to shorter distances consistent with oxidation state increase. Further, the relative intensities for the first and second neighbor are different than those of ORR phase, revealing a different phase. In addition, considerable amplitude is observed between 4-6 Å which originates from multiple scattering as indicated by the structural units. This is an evidence that OER phase has more long range order as compared to ORR or dry sample.

In Figure 4.9 (b) ORR relevent EXAFS curve has been compared with those of model compounds including Ni(OH)$_2$, NaNiO$_2$ and β-NiOOH. As observed in XANES, it does not match any of the reference compounds, likely due to a combination of different phases. Careful examination of the second peak corresponding to the send neighbor shell, reveals a slightly shorter distance as compared to Ni(OH)$_2$. This is another indication that under ORR conditions the catalytic phase comprises a mixture of N$^{2+}$ and Ni$^{3+}$. Comparison of the OER phase is shown in Figure 4.9 (c) with β-NiOOH, γ-NiOOH, and NiPPI. Contrary to the ORR phase, considerable similarities are noticed between the spectra of OER and γ-NiOOH. However, the amplitude of the peak appearing at an apparent distance of ~5.2 Å is smaller for the sample than γ-NiOOH. This peak corresponds to M-(O)$_2$-M-(O)$_2$-M motif and further indicates a layered structure of the sample similar to γ-NiOOH. As noticed in XANES, the catalytic phase has Ni with an average oxidation state slightly less than that in γ-NiOOH. This means that Ni$^{3+}$ content is higher in the
sample as compared to the reference compound. Since Ni$^{3+}$ has stronger Jahn-Teller distortion, higher Ni$^{3+}$ content would lead to reduced amplitude as observed in the sample. Smaller crystallite size could be another reason for reduced amplitude of multiple scattering peak. Also, the peak appears at slightly shorter distance in case of sample, which likely originates due to sample having Mn alongside Ni.
**Figure 4.9:** (a) Fourier transformed EXAFS spectra at n\(i\) K-edge of as-prepared MnNiOx and under ORR and OER conditions. (b) EXAFS trace of sample poised at 0.7 V overlaid with \(\text{Ni(OH)}_2\), NaNiO2 and β-NiOOH. (c) Comparison of OER phase with β-NiOOH, γ-NiOOH, and NiPPI.

### 4.4.3.2 Manganese.

The Fourier-transformed EXAFS traces for as-prepared sample along with the ORR and OER phases have been plotted in **Figure 4.10** (a). Significant structural changes were observed for the catalytic phases under different conditions as seen in figure. For OER phase, considerable intensity is observed between 4-6 Å apparent distance which originates from multiple scattering, suggesting that the catalytic phase has more extended structure under OER conditions. The as-prepared sample did not match any of the measured reference samples, indicating that it might be mixture of phases.

EXAFS of ORR phase is compared with the reference spectra of MnOOH, birnessite and todorokite in **Figure 4.10** (b), and shows strong similarities with birnessite and todorokite confirming the XANES observation. Due to the aforementioned reasons we believe that under ORR conditions catalyst has a birnessite like phase. For similar structures, the FT amplitude is a rough measure of the affluence of structural motif corresponding to each peak. For the first peak in the EXAFS spectra, which corresponds to the nearest neighbor shell, the amplitudes are comparable for the sample and reference birnessite. However, slightly smaller amplitude is observed for the second peak corresponding to the ORR phase as
Figure 4.10: (a) Mn K-edge EXAFS spectra of as-prepared MnNiO\textsubscript{x} and under ORR and OER conditions. (b) EXAFS trace of ORR phase overlaid with Mg\textsuperscript{2+}-birnessite, Todorokite and MnOOH. The sample shows similarities with birnessite phase. (c) Comparison of the MnNiO\textsubscript{x} film poised at 1.8V with β-MnO\textsubscript{2}, λ-MnO\textsubscript{2}, and Todorokite.
compared to birnessite, likely due to relatively diminished structural order beyond the first coordination sphere. As shown in Figure 4.10 (c), which compares the EXAFS spectra of OER phase with reference samples like birnessite and MnO₂, a close resemblance was noticed between the EXAFS spectra of λ-MnO₂ and OER phase which is consistent with the XANES observation. However, the amplitude ratio of the peaks 1 to 2 and 4 to 6 Å are different as compared the closely resembling model compound.

To have a comparative look at local structure of OER phase, the EXAFS traces of the MnNiOₓ at Mn and Ni K-edge have been compared with the closely related model compounds in Figure 4.11 (a). Crystal structures of γ-NiOOH, birnessite and λ-MnO₂ are shown schematically in Figure 4.11 (b). Unlike birnessite and γ-NiOOH which have layered structures, λ-MnO₂ has a spinal structure extending three dimensionally. As indicated by the vertical dashed line (Figure 4.11 a), the first neighbor distances, represented by peak 1, are shorter for Ni than Mn due to higher electronegativity of the former. Peak 4 stems from linear M-(O)₂-M-(O)₂-M motif, whereas peak 3 corresponds to diagonal cation neighbors, as illustrated by the structural fragment in Figure 4.11 (a).
Figure 4.11: (a) Mn and Ni K-edge Fourier transformed EXAFS spectra of MnNiOₓ sample under OER conditions overlaid with λ-MnO₂ and γ-NiOOH. (b) Schematic representation of crystal structures of γ-NiOOH, birnessite and λ-MnO₂.
In layered structures peak 4 has higher amplitude than that of 3, despite originating from longer distance, due to the focusing effect. There are 6 scatterers giving rise to peak 4 in layered structures as well as in $\lambda$-MnO$_2$, however, the “diagonal” neighbors corresponding to peak 3 are only 6 in sheets of layered compounds, whereas such diagonal neighbors are available three dimensionally in $\lambda$-MnO$_2$ and they are 12 in number (2 attached to each of the 6 second neighbors). Therefore, peak 3 has higher amplitude in case of $\lambda$-MnO$_2$ as compare to birnessite or $\gamma$-NiOOH. Since for OER phase the amplitude of peak 3 in Mn K-edge EXAFS is comparable to that of the corresponding peak in Ni K-edge EXAFS, we believe that Mn is mostly in a layered structure along with Ni.

4.5 Conclusions

We have developed a method of detecting XES signal from multiple elements simultaneously by using a wavelength dispersive multi-crystal spectrometer. We have demonstrated the feasibility of this method by applying it to Mn oxide-based bifunctional electrocatalysts. Inclusion of Ni lead to an increase in average oxidation state of Mn under ORR as well as OER conditions. Additionally, reversibility of the electrocatalyst was considerably improved with the incorporation of Ni, most likely due to a layered type structure, both for ORR and OER.

The method described here can be applicable to time-resolved studies of natural and inorganic catalysts, electron transfer pigments, etc. at synchrotron as well as X-ray free electron laser facilities. The instrument is specifically designed for time-resolved applications of XES and X-ray Raman Scattering (XRS) at X-ray Free
Electron Lasers (XFEL) and synchrotron radiation facilities. It will also simplify resonant inelastic X-ray Scattering (RIXS) studies of the whole 2d RIXS plane.

We want to extend this approach to the valence to core region (Kβ2,5 transitions). As these transitions are sensitive to the protonation state of the metal ligand. This will allow to monitor the movements of protons in the bi-metalic system in real time, a process considered to be essential for providing stability to intermediate states in the reaction sequence. These extended studies will be accompanied with improved theoretical modeling of the transitions to better understand the atomic details of the studied reaction steps.

Also, an extension of this approach to lower concentration biological bi-metalic systems (metalloenzymes) is envisioned. This could allow to follow changes in redox and ligation states of the metal centers in metalloenzymes over the respective catalytic cycle.

4.6 References


