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Optical spectroscopy of nanoscale and heterostructured oxides

Tess R. Senty

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OPTICAL SPECTROSCOPY OF NANOSCALE AND HETEROSTRUCTURED OXIDES

Tess R. Senty

**Dissertation submitted to the
Eberly College of Arts and Sciences
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
in
Physics**

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**Morgantown, West Virginia
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**Keywords: Transient Absorption Spectroscopy, Absorption Spectroscopy,
Photoluminescence, FTIR, Photovoltaics, Photocatalysis, Heterostructure
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Abstract

OPTICAL SPECTROSCOPY OF NANOSCALE AND HETEROSTRUCTURED OXIDES

Tess R. Senty

Through careful analysis of a material's properties, devices are continually getting smaller, faster and more efficient each day. Without a complete scientific understanding of material properties, devices cannot continue to improve. This dissertation uses optical spectroscopy techniques to understand light-matter interactions in several oxide materials with promising uses mainly in light harvesting applications. Linear absorption, photoluminescence and transient absorption spectroscopy are primarily used on europium doped yttrium vanadate nanoparticles, copper gallium oxide delafossites doped with iron, and cadmium selenide quantum dots attached to titanium dioxide nanoparticles.

Europium doped yttrium vanadate nanoparticles have promising applications for linking to biomolecules. Using Fourier-transform infrared spectroscopy, it was shown that organic ligands (benzoic acid, 3-nitro 4-chloro-benzoic acid and 3,4-dihydroxybenzoic acid) can be attached to the surface of these molecules using metal-carboxylate coordination. Photoluminescence spectroscopy display little difference in the position of the dominant photoluminescence peaks between samples with different organic ligands although there is a strong decrease in their intensity when 3,4-dihydroxybenzoic acid is attached. It is shown that this strong quenching is due to the presence of high-frequency hydroxide vibrational modes within the organic linker.

Ultraviolet/visible linear absorption measurements on delafossites display that by doping copper gallium oxide with iron allows for the previously forbidden fundamental gap transition to be accessed. Using tauc plots, it is shown that doping with iron lowers the bandgap from 2.8 eV for pure copper gallium oxide, to 1.7 eV for samples with 1 – 5% iron doping. Using terahertz transient absorption spectroscopy measurements, it was also determined that doping with iron reduces the charge mobility of the pure delafossite samples.

A comparison of cadmium selenide quantum dots, both with and without capping ligands, attached to titanium dioxide nanoparticles is performed using a new transient absorption analysis technique. Multiple exponential fit models were applied to the system and compared with the new inversion analysis technique. It is shown how the new inversion analysis can map out the charge carrier dynamics, providing carrier recombination rates and lifetimes as a function of carrier concentration, where the multiple exponential fit technique is not dependent on the carrier concentration. With the inversion analysis technique it is shown that capping ligands allow for increased charge transfer due to traps being passivated on the quantum dot surface.

DEDICATION

To Duncan who never let me give up.

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-Tess R. Senty

TABLE OF CONTENTS

Abstract	i
Dedication	iii
Acknowledgements	iv
Table of Contents	v
CHAPTER 1: Introduction	1
1.1 Introduction and Motivation	1
1.2 Summary of Chapters	9
CHAPTER 2: Sample Preparation and Characterization	10
2.1 Colloidal CdSe Quantum Dot, TiO ₂ Nanoparticle Heterostructure	10
2.2 YVO ₄ :Eu ³⁺	11
2.2.1 Synthesis of YVO ₄ :Eu ³⁺ Nanoparticles	12
2.2.2 Characterization of Nanoparticles	13
2.2.3 Organic Ligands	17
2.3 Delafossites	18
2.3.1 Powders	18
2.3.2 Thin Films	19
2.4 NbO ₂ Thin Films	19
2.5 Chapter Summary	20
CHAPTER 3: Absorption Spectroscopy	21
3.1 Introduction to Absorption Spectroscopy	21
3.2 UV/vis Linear Absorption of QD/TiO ₂ Heterostructure	24
3.3 UV/vis Linear Absorption of CuGa _{1-x} Fe _x O ₂	25
3.4 Bandgap Determination Using Fourier Transform Spectroscopy on Thin Films	30
3.5 Using Fourier Transform Infrared Spectroscopy to Characterize Molecular Vibrations in YVO ₄ :Eu ³⁺	33
3.6 Using Fourier Transform Infrared Spectroscopy to Ensure Organic Ligand Attachment to YVO ₄ :Eu ³⁺	35
3.7 Using Tauc Plot to Determine Bandgaps	36
3.7.1 Using Tauc Plot to Determine Bandgaps	37

3.7.2	Tauc Plot on Delafossite Powders	38
3.8	Chapter Summary	39
CHAPTER 4: Photoluminescence and Photoluminescence Excitation		41
4.1	Introduction to Luminescence	41
4.2	Experimental Techniques	42
4.3	Effect of Capping Ligands on CdSe/TiO ₂ Heterostructure Surface States	43
4.4	Photoluminescence for Understanding Electronic States of YVO ₄ :Eu ³⁺ Nanoparticles	46
4.5	Effects of Photoluminescence on YVO ₄ :Eu ³⁺ with Organic Ligands	50
4.6	Chapter Summary	54
CHAPTER 5: Transient Absorption Spectroscopy		56
5.1	A Brief Introduction to Nonlinear Optics	56
5.2	Introduction to Transient Absorption Spectroscopy	58
5.3	Experimental Techniques	62
5.4	Terahertz Transient Absorption Spectroscopy on Delafossites	68
5.5	Transient Absorption Spectroscopy on YVO ₄ :Eu ³⁺	70
5.6	Exponential Modeling of Transients	72
5.7	Using Transient Absorption Spectroscopy to Understand Charge Dynamics in CdSe/TiO ₂ Heterostructures	74
5.8	Inverting Transients to Understand Concentration Dependent Charge Dynamics	77
5.9	Comparison of Multi-Exponential and Inversion Analysis	92
5.10	Chapter Summary	93
CHAPTER 6: Summary and Conclusion		96
References		99

CHAPTER 1: Introduction

1.1 Introduction and Motivation

From lightbulbs to computers and far beyond, light-based technologies enhance everyday living. Communication has never been faster and more wide-spread. Solar panels are more efficient, providing renewable affordable energy. The medical industry is able to use nanosized materials to help fight against diseases. With continued research and development on new materials, photonic devices can continue to improve our lives. This year in particular, is an exciting year to be publishing a dissertation on photonic devices because the United Nations has proclaimed 2015 to be the International Year of Light and Light-based Technologies.

To develop new photonic devices, there needs to be a full understanding of light-matter interactions within the materials used. With optical spectroscopy techniques, this dissertation develops an understanding of several oxide materials which can be used to harvest solar energy, drive catalytic reactions, tag molecules and much more.

Semiconductor oxides have electrical conductivities between those of a conductor and an insulator and contain at least one oxygen atom. They tend to have a high mobility, and maintain stability in air and water in ambient conditions.^{1,2} Semiconductor oxides can be relatively inexpensive and environmentally friendly due to oxygen being abundant and nontoxic. These properties present a wide range of promising applications. For example, wide bandgap oxides have a high optical transparency and are ideal for light-emitting diodes, thin film transistors and transparent electrodes.³ Narrow bandgap oxides are strongly absorbent and therefore are attractive as solar cell materials.

Harvesting solar energy for photovoltaics (PVs) and photocatalysis has become a major technological challenge when dealing with the current climate changes. With coal and natural gas being major sources of power in the United States, there has been a large push to develop materials which can convert the byproduct of combustion, namely carbon dioxide (CO_2), into reusable fuels. Current technologies for capture and conversion are too costly for large scale use such as in power plants, although by exploiting energy from the sun, photocatalytic reduction of CO_2 into valuable chemicals is a promising technical solution.⁴⁻⁷ PVs provide another potential solution to the current energy crisis by converting readily available sunlight into usable electricity. With PVs, there is no greenhouse gas emission, providing a cleaner source of energy.

To efficiently convert CO_2 into reusable fuels or sunlight directly into electricity, a material must possess strong solar-light absorption, efficient charge separation and transport, and have low charge recombination. In PVs, single-junction cells are restricted to approximately a 30% theoretical efficiency by the Shockley-Queisser limit.⁸ In a simple picture, this loss in conversion efficiency is twofold: (i) lack of absorption of photon energies below the bandgap, and (ii) the inability to use the excess photon energy that results in above bandgap thermalization of hot charge carriers.⁹

Semiconductor heterostructures play a central role in photonics and electronics. In solar-light-harvesting applications for example, when two semiconductor materials with different bandgaps, E_g , are placed together, the operation of the device can be altered through band-gap engineering. This technique has been exploited in tandem PV cells,¹⁰ doubling the $\sim 30\%$ efficiency set for single materials as results from thermalization.^{8,9} With combining two materials into a heterostructure, the relative position of the conduction and valence bands lead to different

types of heterostructures. Type I and II are displayed in Figure 1.1. In type I band alignment, E_{g1} straddles E_{g2} . Here, the smaller bandgap (E_{g2}) lines up within the larger bandgap (E_{g1}) material, allowing electrons and holes to localize within the smaller bandgap material. This type of band alignment is beneficial for high photoluminescence (PL) efficiency, where recombination is desired. In type II alignment, E_{g1} and E_{g2} are staggered, allowing electrons and holes to localize in different materials. This prevents recombination from occurring, therefore is ideal for light harvesting heterostructures, where charge separation is necessary.

FIGURE 1.1 Type I and Type II band alignment for heterostructures.

Taking advantage of bandgap alignment with heterostructuring, wide-bandgap metal-oxide photocatalysts, such as titanium dioxide (TiO_2), can have their light absorption range extended.^{11–13} TiO_2 is a good candidate for PVs and photocatalytic reactions because it is reasonably active, abundant and inexpensive. With the addition of a thin semiconductor photosensitizer (quantum dot [QD] or organic dye) coated on top of TiO_2 nanoparticles, dye-sensitized solar cells (DSSC) provide an increase in light absorption.^{14–19} O'Regan and Gratzel

designed the first n-type DSSC out of TiO_2 nanoparticles, sensitized with a monolayer of ruthenium-based dye.¹⁸ Their work resulted in high-efficiency solar devices at low cost, opening the doors to the next generation solar cells. Sensitizing with QDs provides more tunability of the absorption and greater absorption coefficients than dyes.^{20,21} QDs even present the possibility of harvesting more than one exciton per photon with multiple exciton generation, potentially surpassing the Shockley-Queisser limit.^{22,23} In order for these breakthroughs to succeed, there must be a thorough understanding of the underlying mechanisms.

Both broad spectrum absorption and charge-carrier separation are critical to efficient solar-light harvesting. Successful heterostructures increase photoexcited carrier lifetimes and increase light-to-chemical conversion efficiencies. In practice, the heterostructure interface introduces new trap states and other recombination pathways that limit the overall performance gains. To understand these limiting processes, this dissertation looks at the light-matter interactions of CdSe QDs attached to TiO_2 NPs. CdSe QDs can be adjusted in size to absorb visible to near-infrared photons and have a type II band alignment (Figure 1.1) with TiO_2 . This allows long lived photoexcited electrons to be easily injected into the TiO_2 , improving charge separation and reducing recombination. Using linear UV/vis absorption, luminescence and transient absorption spectroscopy (TAS), the effects of capping ligands on electron transfer in CdSe QD/ TiO_2 heterostructures is studied.

Although QD and DSSC show promising results as affordable alternatives to conventional silicon devices, their efficiencies are still low. According to reports from the National Renewable Energy Laboratory as of 2015, the highest achieved efficiency for DSSC and QDSC are 11.9% and 9.9% respectively. As previously discussed, the QD/ TiO_2 heterostructure device is n-type

where the photocurrent results from electrons being injected from the QDs into the n-type TiO₂ NPs. On the other hand, p-type sensitized solar cells work in the opposite manner, with holes being injected into the p-type semiconductor (or electrons into the QD or dye). Combining an n-type photoanode such as TiO₂, with a p-type photocathode, into a tandem sensitized solar cell can provide an improved open-circuit voltage and increased efficiency.^{24,25}

Research on p-type DSSC is scarce when compared to that of n-type mainly due to the lack of a material with a wide optimal bandgap. NiO is frequently used^{24,26} although its band alignment is very close to the redox potential of commonly used electrolytes and it has low hole mobility.²⁷ Delafossites on the other hand have a high conductivity and can be transparent to the visible spectrum. CuGaO₂ in particular has an electrical conductivity of $6.3 \times 10^{-2} \text{ S cm}^{-1}$ and is 80% transparent to the visible region.²⁸ These properties present a promising solution to finding a wide bandgap, transparent conducting oxide which can be used as a p-type DSSC.

The first delafossite was discovered by Friedel²⁹ in 1873 and classified structurally by Pabst³⁰ in 1946. The material was CuFeO₂ and it was soon discovered that a whole family of oxides existed which shared the same delafossite structure. Delafossites are ABO₂ materials where A is a +1 metal ion and B is a +3 metal ion. They mainly crystallize in the rhombohedral $\bar{R}\bar{3}m$ or hexagonal P6₃/mmc crystalline structures. Whether the B site atom is from the 3A (B, Al, Ga, In, or Tl) or 3B (Sc, Y, La or Ac) group in the periodic table, defines what the ground state structure of the material will be.³¹ If the B site atom is from the 3A group, the material prefers to crystallize in the rhombohedral form, while if it is from the 3B group, the material prefers to crystallize in the hexagonal form.

CuGaO₂ delafossites are p-type with a large bandgap of ~3.2 eV. Since Ga is in the 3A group, CuGaO₂ prefers a rhombohedral structure. Due to the wide optical bandgap, excellent hole mobility, stability in aqueous solution, and other versatile properties, CuGaO₂ is primarily studied for use as a transparent conducting oxide.^{32,33} A lower fundamental bandgap accompanies the wide optical bandgap,³³ however inversion symmetry forbids the optical transitions across the fundamental bandgap. By doping CuGaO₂ with a second B-site element, inversion symmetry can be broken and the bandgap of the material can be drastically reduced,³⁴ allowing bandgap tunability. In order for delafossites to be useful in photovoltaics, first there must be an understanding of the bandgap and how doping affects the structure.

Doping CuGaO₂ with 5%, 10%, 15% and 20% concentrations of Fe shifts the absorption edge from 2.55 eV for pure CuGaO₂ to 1.5 eV for Fe doped samples.³⁵ Introducing Fe into the system does not affect the conduction band, but introduces strain in the system. This causes a break in the inversion symmetry of the crystalline lattice, making the previously forbidden electronic transitions accessible.

Theoretical studies of CuGa_{1-x}Fe_xO₂ with Fe doping between $0.00 < x < 0.05$ shows that below $x = 0.05$, Fe atoms prefer to sit in the same crystallographic plane, although at $x = 0.05$, Fe atoms prefer to maximize distance between other Fe atoms.³⁶ This does not allow the crystal to minimize strain by lessening the number of planes containing Fe atoms. The local strain from substituted Fe atoms then becomes a global effect. Calculated total and partial density of states show that increasing the Fe substitution has no significant change on the electronic structure and the change in absorption is due to deformation of the Cu – O bonds as x increases.³⁶ To further understand the mechanisms at work in this system, experimental

diffuse reflectance and THz TAS data for $\text{CuGa}_{1-x}\text{Fe}_x\text{O}_2$ at low Fe concentrations, ($x=0.01, 0.02, 0.03, 0.04, 0.05$) are performed.

Another issue current PV technologies exhibit is low external quantum efficiencies for UV photons. These high energy photons, which are incident on a material lose most of their energy due to thermalization. For example, silicon which has a bandgap near 1.1 eV will lose about 30% of the incident light energy due to relaxation to the band edge. By converting high energy photons to visible, where PV materials are much more responsive to solar conversion, the efficiency of the solar device can be improved.³⁷ This can be achieved with the use of luminescent down-shifting (LDS) materials. With the addition of a LDS layer into a solar device, high energy photons are absorbed by the LDS layer and re-emitted at lower energies where the device exhibits a much higher response.^{38,39} Materials ideally used for LDS layer will have a high absorption coefficient, a narrow emission band which matches the peak sensitivity response of the device, a wide absorption band in the region where the device has low external quantum efficiency, and separation between absorption and emission bands to avoid re-absorption.³⁹ Rare-earth ions have a high luminescent quantum efficiency but low absorption coefficients. Low absorption can be improved by placing rare-earth ions into a host material with a large absorption coefficient which then exhibits efficient transfer to the rare-earth ion.

Europium doped yttrium vanadate ($\text{YVO}_4:\text{Eu}^{3+}$) is a promising LDS material due to the high absorption coefficient of YVO_4 . $\text{YVO}_4:\text{Eu}^{3+}$ also exhibits efficient transfer of electrons from the host to Eu^{3+} ion which then emits a strong red emission near 620 nm. Amorphous and crystalline Si solar cells have a maximum spectral sensitivity in the red region of the solar spectrum.⁴⁰ By converting the low absorption UV photons into red photons with a $\text{YVO}_4:\text{Eu}^{3+}$ LDS layer,

electron absorption can be increased. Kumar et al.⁴⁰ showed a 7.7% increase in efficiency of a commercial silicon solar cell when a $\text{YVO}_4\text{:Eu}^{3+}$ nanophosphor layer was added to the device.

$\text{YVO}_4\text{:Eu}^{3+}$ also has promise for applications in medical, opto-electronic and solid-state lighting realms.^{41–44} Some biomedical applications seek to use the luminescence of multifunctional nanostructures for targeted drug delivery, labeling or sensing with magnetic manipulation for separation or capture of cells, proteins and nucleic acids. With these applications, it is essential that the addition of one function does not hinder another. For example, multifunctional nanoparticles (NP) consisting of magnetic cores and PL shells have been demonstrated, using Fe cores coated with rare-earth-doped YVO_4 as a luminescent shell.⁴⁵

The advantage of rare-earth-doped crystals in biological applications is their low toxicity compared to some colloidal QDs,⁴⁶ strong luminescence properties of common ions such as Eu^{3+} , Lu^{3+} , and Tm^{3+} , and background-free emission due to the necessity of indirect excitation via the host material.^{47–53} These latter properties are also one of the reasons why rare-earth, particularly lanthanide, doped crystals are used for laser materials and optoelectronics.^{41–43} These properties are also promising for use as luminescent nanothermometers.^{54,55} $\text{YVO}_4\text{:Eu}^{3+}$ in particular has been shown to have a temperature-dependent linewidth,⁵⁶ which can then be exploited to achieve a thermal sensitivity on the nanometer scale. It has been found that 5% doping of Eu^{3+} ions in YVO_4 leads to strong red PL close to 620 nm.⁴⁹ $\text{YVO}_4\text{:Eu}^{3+}$ has several other emission lines, including some between 700 – 900 nm,⁵⁷ which corresponds to the first biological window.^{58,59}

Because these materials appear ideally suited for nanoscale biomedical applications, it is important that they bind to biomolecules.⁶⁰ One possible method of achieving strong binding between the inorganic YVO_4 and the organic biomolecules is to use aromatic linker molecules. For use in PVs, it is essential to understand possible quenching mechanisms and electron dynamics so as to keep the PL quantum efficiency high for efficient charge transfer. To understand these mechanisms, the luminescent properties, electron dynamics and possible quenching mechanisms of $\text{YVO}_4:\text{Eu}^{3+}$ are studied throughout this dissertation.

1.2 Summary of Chapters

Chapter 2 presents an outline of the synthesis procedures of the samples which are studied throughout this work. An understanding of the crystal structures is also presented along with characterization of the materials. Linear absorption techniques with ultraviolet, visible and infrared wavelengths are discussed on several samples in Chapter 3. The use of Tauc plots to determine the bandgap of materials is also presented. Chapter 4 describes the fluorescence of CdSe QDs and measures the radiative lifetime. It is discussed how removing capping ligands from the QDs quenches the fluorescence. The photoluminescence of $\text{YVO}_4:\text{Eu}^{3+}$ NP with and without attached organic ligands is also presented. It is described how certain organic ligands can quench the PL therefore should be avoided. Chapter 5 presents a description of TAS using various probe wavelengths to look at different excitation pathways and their dynamics. Terahertz TAS is performed on $\text{CuGa}_{1-x}\text{Fe}_x\text{O}_2$ delafossites to measure how the conductivity changes with increasing Fe concentrations. A new model for analyzing TAS data is proposed and then compared to standard models currently used. The model is described using CdSe/ TiO_2 heterostructures. TAS measurements on $\text{YVO}_4:\text{Eu}^{3+}$ samples are also discussed.

CHAPTER 2: Sample Preparation and Characterization

2.1 Colloidal CdSe Quantum Dot, TiO₂ Nanoparticle Heterostructures

The CdSe/TiO₂ heterostructures linked with 3-mercaptopropionic acid (MPA) were prepared by Congjun Wang at the National Energy Technology Laboratory in Pittsburgh, PA as outlined in Senty et al.⁶¹ The MPA linking caps were removed from the heterostructures by treating them with hydrazine as described below, and a comparison is done of the electron dynamics between with and without MPA linking caps. Heterostructure samples were prepared in an N₂ purged glove box. TiO₂ powder (Evonik, Aeroxide® TiO₂ P25) was placed in ~5 ml of 0.14 MPA in anhydrous acetonitrile. The solution was gently stirred for 2 hours and then kept inside the glove box overnight. The mixture was centrifuged, and TiO₂ powder was washed repeatedly with methanol to remove any free MPA molecules.

Commercially purchased 5.0 nm sized CdSe QDs in toluene were cleaned twice by precipitation with methanol, and then re-dissolved in small amounts of toluene. The MPA treated TiO₂ powder was dispersed in small amounts of toluene to which the CdSe QD solution was slowly added under gentle stirring. The mixture was kept in the glove box for 2 hours, centrifuged and then the powder was rinsed with methanol and dried under vacuum.

Linking caps were removed by putting the MPA treated CdSe/TiO₂ samples in 1 molar hydrazine in ethanol for 2 hours to remove the organic capping molecules. After treatment, the powders were rinsed with large amounts of methanol and then dried under vacuum.

For diffuse reflectance, fluorescence and transient absorption measurements described in the following chapters, the heterostructure and QD samples were prepared by taking

approximately, 1 mg of sample powder (or 58 μL for liquid QDs), mixing it with 100 mg of KBr and pressing it into a powder matrix in the shape of a disk with 0.1 mm thickness. All experiments were performed in ambient conditions.

2.2 $\text{YVO}_4\text{:Eu}^{3+}$

According to the International Center for Diffraction Database (ICDD), bulk YVO_4 has a wakefieldite or tetragonal zircon structure. It belongs to the space group $D_{4h}^{19}\text{-I}4_1/\text{amd}$, with unit cell parameters $a = b = 7.1183 \text{ \AA}$, $c = 6.2893 \text{ \AA}$, $Z = 4$ ⁶² (Figure 2.1). When europium (Eu) is

FIGURE 2.1 Crystal structure of YVO_4 with Y represented in green, V in blue and O in red. Created using VESTA.⁶³

added to the crystal structure, it takes the place of the yttrium (Y) ion and the crystal structure remains in the same state. The ionic radius of Y is $1.01 \text{ \AA}$ and that of Eu is $1.07 \text{ \AA}$.⁶⁴ These ionic radii are close enough that major distortion of the crystal structure is not expected. Here, eight oxygens located at the vertices of a tetragonal dodecahedron surround the europium ion and provide a D_{2d} local site symmetry. The $^5\text{D}_0 - ^7\text{F}_2$ electric-dipole transition is highly sensitive to

the local environment, only being allowed when Eu occupies a site without an inversion center, as is found at the D_{2d} site.⁵¹ This transition provides the characteristic strong red emission of YVO₄:Eu³⁺.

2.2.1 Synthesis of YVO₄:Eu³⁺ Nanoparticles

Colloidal YVO₄: Eu³⁺ nanoparticles (NP) were synthesized by Mohita Yalamanchi and Tess R. Senty at West Virginia University, using a wet-chemical-synthesis procedure outlined by Riwotzki and Haase.^{65,66} This straight forward method produces crystallized NPs directly from aqueous solutions. Here we create a 5% Eu³⁺ dopant level which is known to produce the maximum PL in bulk and NPs.^{49,65,67,68} This optimum PL is a result of the tradeoff between concentration quenching and radiative recombination. If too few of Eu³⁺ ions are present, the probability of energy transfer between the vanadate host and Eu³⁺ ion decreases, decreasing the radiative recombination. Alternatively, if there are too many Eu³⁺ ions, the increase in non-radiative recombination centers decreases the quantum yield.⁴⁹

Riwotzki and Haase's synthesis procedure⁶⁵ is outlined as follows: 30 mL of distilled water was mixed with 3.413 g of Y(NO₃)₃·6H₂O and 0.209 g of Eu(NO₃)₃·6H₂O which were dissolved completely. 1.38 g of Na₃VO₄ was completely dissolved in another 30 mL of distilled water. The two solutions were mixed together in a Teflon vessel and stirred for 20 min. From this, a white suspension with a pH value of approximately 5 was formed. This suspension was placed into an autoclave and heated to 200°C. After the sample cooled, it was placed in a centrifuge for 10 min, and everything but the precipitate was discarded. The precipitate was mixed with 3.22 g of aqueous 1-hydroxyethane-1,1-diphosphonic acid and allowed to dissolve in 40 mL of distilled water. Under the hydrothermal treatment, Y(OH)₃ forms within the solution due to excess

yttrium ions. To dissolve $\text{Y}(\text{OH})_3$, HNO_3 was added to the suspension until a 0.3 pH was reached. The solution was then stirred for 1 hour. The solution turned a reddish color due to the formation of V_2O_5 . Concentrated NaOH was added to the suspension until approximately a 12.5 pH was reached. At this pH, the reddish V_2O_5 react to form sodium vanadate and all excess metal ions form soluble complexes within the diphosphonic acid. This allows the separation of $\text{YVO}_4:\text{Eu}^{3+}$ NPs from the excess materials. The solution was placed in a capped vessel and stirred overnight. The resulting white suspension of $\text{YVO}_4:\text{Eu}^{3+}$ was centrifuged for 10 min and everything else was discarded. For FTIR, PL and PLE measurements, powdered $\text{YVO}_4:\text{Eu}^{3+}$ samples were mixed with KBr at a sample to KBr ratio of 5:95, then compressed into 0.5 mm thick disks.

For transient absorption measurements, powdered $\text{YVO}_4:\text{Eu}^{3+}$, $\text{YVO}_4:\text{Eu}^{3+}/\text{BA}$ and $\text{YVO}_4:\text{Eu}^{3+}/\text{DHBA}$ were independently mixed with anhydrous terpineol, mixture of isomers, purchased from Sigma-Aldrich at a concentration of 0.2 g/mL. Mixtures were stirred overnight to form a homogenous suspension. The suspension was dropped onto glass microscope slides, and wiped with a razor blade to form a thin film. The films were then allowed to dry in ambient conditions.

2.2.2 Characterization of Nanoparticle Crystalline Structure

The NP crystal structure was characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM) images. XRD was taken with a Rigaku diffractometer, equipped with CuK_α source at a wavelength of 1.54185 Å and supported by the ICDD and Jade 9 software. XRD provides the crystal structure by measuring x-rays that are diffracted from the crystal plates.

Bragg's Law, $2d \sin \theta = n\lambda$, is used to determine the distance, d , between atomic layers in

a

crystal, where n is an integer representing the diffraction order, λ is the incident x-ray wavelength, and θ is the angle of incidence. Figure 2.2 demonstrates Bragg's Law on a periodic crystal.

FIGURE 2.2 Bragg's Law on a periodic crystal structure.

XRD patterns captured from the $\text{YVO}_4\text{:Eu}^{3+}$ NPs are displayed in Figure 2.3 (a), and comparison to Figure 2.3 (b), shows a perfect match in angular position and intensity to the wakefieldite crystalline structure produced from ICDD. This verifies that synthesis produced the correct crystal structure.

FIGURE 2.3 (a) X-ray diffraction pattern from the as-grown $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles. (b) Expected peak structure of wakefieldite given in the International Center for Diffraction Database. Figure was modified from Senty *et al.*⁶⁹

The average crystalline size was measured using the Scherrer equation, $\tau = K\lambda / (\beta \cos \theta)$, where K is a dimensionless shape factor, λ is the X-ray wavelength, β is the line broadening at the full-width half maximum (FWHM) and θ is the Bragg angle. The Scherrer equation relates the size of NPs (τ) to the broadening of their XRD diffraction peaks (β). From this, it was estimated that the average crystalline size was 17 nm and the structure had a single chemical phase. Based on initial starting weights of the chemicals used in synthesis, this suggests the

expected 5% Eu concentration allows for uniform substitution of the Eu^{3+} ions within the YVO_4 host.

FIGURE 2.4 Transmission electron micrographs of samples with (a) 20 nm and (b) 4 nm scale bars. Figure was modified from Senty *et al.*⁶⁹

Figure 2.4 shows the TEM images that were captured using a JEOL JEM-2100 LaB6 at two different magnification levels. The average circular NP shape can be seen from Figure 2.4 (a), and in the higher magnification image in Figure 2.4 (b), the tetragonal morphology of the crystal structure is clearly shown. Using ImageJ software, the minor axis of a small distribution of NPs was measured within the TEM images to give an average size of 16 nm, in excellent agreement with the crystalline size calculated from the Scherrer equation. The distribution of NP size is displayed within the histogram of Figure 2.5 where a mean aspect ratio was calculated to be 1.58 with the standard deviation of 0.28.

FIGURE 2.5 Nanoparticle size dispersion histogram measured from diameters in TEM images. Figure was modified from Senty *et al.*⁶⁹

2.2.3 Organic Ligands

Inorganic $\text{YVO}_4\text{:Eu}^{3+}$ NPs cannot be used in biomedical applications unless they can be bound to organic biomolecules. Since organics cannot be directly linked to the metal surface of $\text{YVO}_4\text{:Eu}^{3+}$ NPs, an aromatic linker molecule must be attached to the surface. The native metal-hydroxyl bonds produced from chemical synthesis act as anchor points for these aromatic linkers. Chemical treatments were performed via metal-carboxylate coordination, to attach three aromatic linker molecules: benzoic acid (BA), 3-nitro-4-chlorobenzoic acid (NCBA) and 3,4-dihydroxybenzoic acid (DHBA).⁷⁰ For each treatment, 500 mg of BA, NCBA or DHBA was

added to a suspension of 50 mg $\text{YVO}_4:\text{Eu}^{3+}$ NPs in 5 mL anhydrous N,N-dimethylformamide and 5 mL anhydrous dichloromethane. The suspension was mechanically shaken at room temperature. After 48 hours, the solid complex was collected by a suction filter and dried by vacuum.

2.3 Delafossites

Delafossite crystals have a chemical formula ABO_2 . A is an $+1$ metal cation (e.g. Na, Cu and Ag) while B is a Group III metal (e.g. Fe, Al and In). The crystalline structure of delafossites can be found in either rhombohedral space group $\bar{R}3m$ when B is in group IIIA, or hexagonal space group $P6_3/mmc$ when B is in group IIIB³⁵. Both CuGaO_2 and CuFeO_2 , studied here, belong to the rhombohedral space group $\bar{R}3m$. Lattice parameters for CuGaO_2 and CuFeO_2 are $a=2.980\text{\AA}$ and $c=17.100\text{\AA}$,^{33,34} and $a=3.03\text{\AA}$ and $c=17.09\text{\AA}$,⁷¹ respectively. It has been shown that bandgap modification can occur by alloying Cu-based delafossites, thereby increasing optical absorption at lower energies,³⁴ as will be discussed in detail in Chapter 3.

2.3.1 Powders

Delafossite powders of CuGaO_2 , $\text{CuGa}_{1-x}\text{Fe}_x\text{O}_2$ and CuFeO_2 were synthesized by Jonathan Lekse at the National Energy Technology Laboratory in Pittsburgh, PA as described in Lekse *et al.*³⁵ The chemicals used for synthesis were copper(I) oxide (Cu_2O), 99.9% purchased from Strem; gallium oxide (Ga_2O_3), 99.99% purchased from Alfa Aesar; and iron (III) oxide (Fe_2O_3), 99+% purchased from Aldrich. Depending on the desired Fe doping concentration of 0-5%, the correct stoichiometric mixtures of Cu_2O , Ga_2O_3 and Fe_2O_3 chemicals were ground under acetone for 15 min where the acetone was then allowed to evaporate. The resulting mixtures were then pressed into pellets and heated in a tube furnace under flowing argon gas from room

temperature to 1100 °C in 24 hours. Once heated, the samples were held at 1100°C for 48 hours and finally allowed to cool to room temperature for 3 hours.

2.3.2 Thin Films

CuFeO₂ thin films were synthesized by Toyenath Joshi at West Virginia University onto an Al₂O₃ (00.1) substrate as outlined in Joshi et al.⁷² Substrates were pre-cleaned and annealed at 1200 °C for 2 hours in air allowing for step-and-terrace surface quality. Using a stoichiometric polycrystalline CuFeO₂ target from Shanghai Optics, CuFeO₂ films were deposited onto the Al₂O₃ substrate with a Neocera PLD system with a KrF excimer laser at 248 nm, from Coherent, Inc. The base pressure of the vacuum chamber was approximately 10⁻⁸ Torr. O₂ gas was introduced into the chamber during growth and controlled by a mass flow controller. The distance from the target and substrate was kept at 7.3 cm and the energy density at the target was approximately 2 J/cm². The pulse repetition rate was set to 2 Hz. The surface quality of the substrates and films were monitored using an *in situ* Reflection High-Energy Electron Diffraction (RHEED) system from STAIB Instruments.

2.4 NbO₂ Thin Films

NbO₂ films were grown on a pre-polished Al₂O₃ (0001) substrate by Toyenath Joshi at West Virginia University, using pulsed laser deposition from a ceramic Nb₂O₅ target.⁷³ The target to substrate distance was kept at 7.3 cm and the KrF laser energy density at the target was approximately 2 J/cm², with a pulse repetition rate of 5 Hz. The base pressure of the vacuum chamber was 10⁻⁸ Torr, and films were grown at a substrate temperature of 650 °C in a 7% O₂, 93% Ar gas mixture atmosphere with the total pressure ranging between 1 and 20 mTorr. The surface quality of the substrates and films were monitored using *in situ* RHEED.

2.5 Chapter Summary

Synthesis methods were outlined for CdSe/TiO₂ heterostructures, YVO₄:Eu³⁺ NPs, YVO₄:Eu³⁺ NPs with attached organic ligands, delafossite powders and thin films, and NbO₂ thin films. 5.0 nm sized CdSe QDs were synthesized both with and without capping ligands and attached to TiO₂ NPs. The crystalline structure and NP sizes for YVO₄:Eu³⁺ were determined to be approximately 16 nm using TEM images and XRD. It was demonstrated that aromatic linker molecules of benzoic acid, 3-nitro-4-chlorobenzoic acid and 3,4-dihydroxybenzoic acid can be attached to the surface of the YVO₄:Eu³⁺ NPs, replacing the native surface molecules in the as-grown samples. It was discussed that delafossite powders can be made of CuGaO₂ with Fe dopings between 0-5%. Finally, it was shown that thin films of CuGaO₂ and NbO₂ can be grown with pulsed laser deposition. Experimental techniques are demonstrated on the above mentioned samples throughout the following chapters.

Chapter 3: Absorption Spectroscopy

3.1 Introduction to Absorption Spectroscopy

Absorption spectroscopy gives insight into the molecular makeup and band structure of materials. Different regions of the electromagnetic spectrum will give an understanding of the electronic structure or types of molecules present. Incident photons, which have energies that match the energy difference between electronic transitions or molecular vibrations within a material will be absorbed (Figure 3.1). Mid- to far-infrared wavelengths have a low energy which can cause a change in a molecule's vibrational energy but may not be strong enough to produce an electronic energy transition. When these wavelengths are absorbed, it causes vibrational and rotational excitation of groups of atoms, allowing for the identification of molecules which are present (Figure 3.1).

FIGURE 3.1 Simplified diagram displaying that absorption of ultraviolet and visible light lead to electron orbital changes while absorption of infrared light leads to molecular rotations and vibrations.

Electrons typically absorb ultraviolet (UV) and visible (vis) wavelengths therefore UV/vis absorption gives an understanding of the electronic structure (Figure 3.1). As two atoms approach each other, there will be an overlap and coupling of the atomic wavefunctions (Figure 3.2 (a)), forming a new hybridized orbital (Figure 3.2 (b)). As more atoms are brought together, the molecular orbitals continue to extend, each of which form discrete energy levels. If enough atoms are brought together, eventually a bulk material will form. With this many atoms, the energy levels which were previously discrete states, are so close together that they form a continuum of states (Figure 3.2 (c)). Bandgaps are formed in regions where there are no allowed energy states. This forms the basis of band diagrams where each of the energy levels across the crystal structure can be mapped out. Due to the continuum of states above the bandgap within materials, electromagnetic waves with energies greater than the bandgap will be absorbed. By looking at the onset of absorption, the bandgap of materials can be determined.

FIGURE 3.2 (a) Energy versus lattice constant spacing displaying how bands form as nuclei approach each other. From Grundmann.⁷⁴ (b) Blending of atomic orbitals forms hybridized orbitals. (c) The discrete levels of single atoms form continuums of hybridized states within solids.

Beer's law relates material properties with the attenuation of light, and defines the absorption coefficient (α)

$$A = -\log_{10}(I/I_0) = \epsilon c l \quad (3.1)$$

Here, A is the absorbance, and I and I_0 are the incident and transmitted light intensity, respectively. The absorption coefficient can be determined if the sample path length (l),

concentration (c) and molar attenuation coefficient (ϵ) are known. As seen from Beer's

law,

when photons with certain energies are absorbed into the sample, the light that gets to the spectrometer will be reduced. Below the bandgap, there will be no light absorption because the energy is not strong enough to excite electrons into higher states. As soon as the bandgap energy is reached, the absorption will quickly rise.

Spectroscopy in general, passes radiation (UV, vis, infrared (IR), etc.) through a sample, where some of the radiation is absorbed and some is transmitted. Absorption of radiation causes a change in the dipole moment, forcing an electron or molecule into an excited state. UV/vis wavelengths cause an electron to be excited into an outer orbital, as shown in Figure 3.1. Scanning a monochromator across all wavelengths allows for the energies of absorption to be determined, aiding in the understanding of the electronic structure.

IR wavelengths on the other hand, cause a molecule to be excited from a vibrational ground state to the first excited state (Figure 3.1). Each molecule has a unique IR absorption due to molecular vibrations. This allows for identification of what types and amount of molecules are present.⁷⁵ IR spectroscopy faces difficulties when it comes to slow scanning times and detection

using dispersive instruments like a diffraction grating in a monochromator. Instruments using Fourier transform do not separate individual wavelengths, but instead allow the beam with a set of wavelengths to reach the detector by replacing the diffraction grating with a Michelson interferometer. Here, the beam is split into two beams with different path lengths. Depending on their path length, when the two beams are recombined, they will either interfere constructively or destructively. Collecting data at several different path lengths, produces an intensity which is path length dependent. Then, taking a Fourier transform of the signal produces an energy dependent spectrum.^{75,76}

3.2 UV/vis Linear Absorption of QD/TiO₂ Heterostructures

To characterize C-CdSe QDs, UC-CdSe/TiO₂, and C-CdSe/TiO₂ samples, and understand where the first exciton peak is located, diffuse reflectance spectroscopy measurements were performed, using a Perkin Elmer Lambda 1050 UV/vis/NIR spectrometer equipped with a Labsphere 150 mm integrating sphere. The absorbance was calculated by taking 1-R, where R is the diffuse reflectance. From the absorbance measurements, the first exciton peak of the 5.0 nm sized CdSe QDs was found to be near 2.03 eV, as expected (Figure 3.3). After QDs were attached to TiO₂ NPs both with and without capping ligands, the first exciton peak remained the same. It can be noted from Figure 3.3 that the absorbance for C-CdSe/TiO₂ has a decreased strength compared to C-CdSe QDs and UC-CdSe/TiO₂. This decrease in absorption strength is attributed to the amount of C-CdSe/TiO₂ in the KBr matrix being slightly smaller than the other two samples.

FIGURE 3.3 Linear absorbance of C-CdSe QDs (black) C-CdSe/TiO₂ (red) and UC-CdSe/TiO₂ (blue). Figure modified from Senty *et al.*⁶¹

3.3 UV/vis Linear Absorption of CuGa_{1-x}Fe_xO₂

To understand the effects of Fe doping on CuGaO₂, the absorption of 0-5%, 10% and 100% Fe doping were measured using a Perkin-Elmer Lambda 1050 dual-beam spectrometer. CuGaO₂ has a wide optical bandgap although there is a fundamental bandgap which is much lower.³³ Inversion symmetry causes the fundamental bandgap to be forbidden. The absorbance of pure CuGaO₂ was found to coincide with previous theoretical and experimental results,^{28,33,35} having a prominent absorption feature near 2.5 eV (Figure 3.4). Studies show that by doping with a second B-site element, inversion symmetry can be broken and the bandgap of the material can

be drastically reduced.³⁴ This is seen in Figure 3.4. As Fe atoms are introduced to the system, the absorption edge shifts quickly to the left decreasing the absorption onset to 1.5 eV at 5% Fe doping. The strength in absorption slowly increases as the Fe concentration increases, with the most prominent jump occurring between 4% and 5% Fe concentrations. The absorption edge for CuFeO₂ is even lower in energy than the doped structures with a first pronounced peak around 0.75 eV and a second peak near 1.25 eV, agreeing with earlier bandgap measurements.^{35,72,77} At or near 5% Fe doping, the localized strain on the system from individual Fe atoms becomes a globalized strain effect, causing the observed large shift in absorption. Haycock *et al.*³⁶ discusses that during doping, Fe atoms prefer to be in positions so as to minimize

FIGURE 3.4 Absorbance of CuGa_{1-x}Fe_xO₂ for different Fe concentrations (0-5%, 10% and 100%).

the strain on the system. For low concentrations of Fe, this is achieved when Fe atoms settle within the same crystallographic plane. At 5% doping, the concentration is high enough that the Fe atoms cannot maximize Fe-Fe distance while remaining in the same plane. At this concentration, the number of Fe atoms is enough that their positioning in the system results in a global strain.

To further understand the observed changes in absorption for increasing Fe doping, the allowed selection rules must be discussed. The Laporte selection rule states that for a molecule which is centrosymmetric, a transition is allowed if there is a change in the parity between transitions. The Laporte selection rule is a product of the electric-dipole transition moment vanishing, unless the integrand is invariant under all symmetry operations of the molecule.⁷⁶

Figure 3.5 (a) demonstrates the Laporte selection rule pictorially. Here, r represents the dipole which is odd. On the left hand side of Figure 3.5 (a), both the final and initial states are

oscillatory, therefore $\langle \text{odd} | \text{odd} | \text{odd} \rangle = 0$ and the electric-dipole transition vanishes. In contrast, the two columns on the right display the initial state as linear or a discrete distribution, making

$\langle \text{odd} | \text{odd} | \text{even} \rangle \neq 0$, allowing the transition to occur.

Figures 3.5 (b-f) are calculated charge density plots within the crystal structure. The calculations are performed using FIREBALL's tight binding density functional code. FIREBALL is a self-consistent density functional theory code that is based on the Harris-Foulkes^{78,79} functional and makes use of an ab-initio tight-binding molecular dynamics (TBMD) simulation technique.⁸⁰ For this work, a minimal basis set for O($r_c = 3.4, 3.8$), Fe($r_c = 5.3, 5.8, 4.7$), Cu($r_c = 5.1, 5.6, 4.6$), and Ga($r_c = 4.8, 5.7$) are used, adding a $4p^0$ -state to the Fe

and Cu ground state configurations; r_c values are the wavefunction cutoff lengths (in atomic units) for the s, p, and d orbitals.

FIGURE 3.5 (a) Pictorial representation of Laporte selection rules. (b-f) Charge density distribution plots. (g-i) Band diagrams displaying forbidden and allowed transitions according to Laporte selection rules.

Calculations are performed on a rhombohedral CuGaO₂, $6 \times 6 \times 1$ supercell consisting of 432 atoms created using the non-primitive equivalent hexagonal cell (12 atoms). For each

structure, an appropriate number of Ga atoms are replaced with Fe atoms, and the lattice vectors are scaled according to Vegard's Law

$$\text{Cu}_{1-x}\text{Fe}_x\text{GaO}_2 = (1-x)\text{CuGaO}_2 + x\text{CuFeO}_2 \quad (3.2)$$

where a is the lattice constant and x is the doping fraction. The optimized constants for FIREBALL as well as the initial experimental lattice constants are displayed in Table 3.1.

TABLE 3.1 Experimental and Optimized Lattice Constants for CuGaO₂ and CuFeO₂

		a	c	a_r	A
CuGaO ₂	Experimental	2.975 Å	17.154 Å	5.970 Å	28.854°
	Optimized	2.945 Å	16.982 Å	5.911 Å	28.852°
CuFeO ₂	Experimental	3.0351 Å	17.166 Å	5.984 Å	29.380°
	Optimized	3.0503 Å	16.909 Å	5.905 Å	29.936°

For 0% - 5% Fe concentrations, the charge density for the calculated lowest unoccupied molecular orbital (LUMO) has an oscillatory behavior. Due to their similarities, only 5% Fe concentration is shown in Figure 3.5 (b). As demonstrated in Figure 3.5 (c), the optical transition, has a smooth, or linear charge density distribution across the crystal lattice. The density is mainly surrounding the Ga and O atoms. Again, this smooth behavior is seen across all concentrations therefore only 5% Fe is shown. The charge distributions of the highest occupied molecular orbital (HOMO) for 0%, 1% and 5% Fe concentrations are shown in Figures 3.5 (d), (e), and (f) respectively. For 0% Fe concentration, the charge density oscillates across each Cu atom. The frequency of oscillations are much quicker than seen in the LUMO charge distribution where the density is distributed across all atoms. This suggests that the HOMO to optical transition is allowed, while the HOMO to LUMO is forbidden. A pictorial representation of these transitions are shown in Figure 3.5 (g). In contrast, the charge density of the HOMO for 1 – 5% Fe consist of discrete clusters of charge surrounding the Fe atoms. The discrete regions change the parity, allowing the transition between HOMO and LUMO

(Figure 3.5 (h-i)). By changing the parity, once Fe is added into the system, it opens up another transition which was previously forbidden. This provides the shift in absorption to lower energies seen in Figure 3.4.

3.4 Bandgap Determination Using Fourier Transform Spectroscopy on Thin Films

Optical reflection/transmission measurements were conducted in ambient conditions on NbO₂ thin films grown at 1 mTorr and 20 mTorr, using Fourier-Transform spectroscopy with a halogen light source and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The spectra were collected with a 0.001 eV resolution between 0.3 eV to 1.8 eV. Both reflection $R(\lambda)$ and transmission $T(\lambda)$ were measured and displayed in Figure 3.6. While taking reflection measurements, some collection light is lost. To correct for this, a slight offset was subtracted from the absorption data.

Absorption measurements of Figure 3.6 allow for identification of NbO₂ for the sample grown at 1 mTorr and Nb₂O₅ for the sample grown at 20 mTorr pressures. It is clear in Figure 3.6 that there is no absorption within the wavelength collected for the sample grown at 20 mTorr. Nb₂O₅ phase has a bandgap between 3.5 to 4.8 eV^{81,82} therefore an increase in the absorption would not be seen within this photon energy range. Although for the sample grown at 1 mTorr, there is a clear increase in the absorption within this photon energy range, indicating the onset of a band edge. NbO₂ phase is known to have a bandgap between 0.3 to 1.0 eV.^{83–87} The absorption measurements displayed within Figure 3.6 provide evidence of a bandgap within this range. The small, broad peaks near 0.65 eV and 0.9 eV are due to water absorption and can be disregarded.

In a perfectly ordered system, the band edge will appear as a clear sharp increase in absorption. Due to the formation of localized states within the band tails, the onset of absorption may not be sharp but actually exponential. This exponential growth below the band edge is known as the Urbach tail and is due to traps and defects within the sample.^{74,88,89} The absorption spectra of the Urbach region is represented by the exponential equation

$$\alpha(\hbar\omega) \propto \exp[(\hbar\omega - E_g)/E_u] \quad (3.3)$$

where E_g is the bandgap energy and E_u is the Urbach parameter.⁷⁴ The Urbach parameter helps describe the amount of distortion to the band edge where localized states have formed, decreasing the size of the gap. This energy represents a transition from the localized band tail to the extended band.

The absorption on NbO₂ in Figure 3.6 displays this exponential like behavior. NbO₂ was fit to equation 3.3, giving an Urbach parameter, $E_u = 0.2$ eV, and an energy bandgap, $E_g =$

0.58 eV. The fit is shown in Figure 3.6 as a dashed-orange line. The estimated bandgap is well within the range of reported values.⁸³⁻⁸⁷ The Urbach parameter measures the energy width of the bands that extend below or above the conduction or valance bands. A larger Urbach parameter makes for a smaller than expected bandgap. The Urbach parameter calculated here is quite large in comparison to the size of the bandgap, indicating the presence of impurities which are disturbing the electronic structure.⁹⁰ Larger than bulk Urbach parameters are expected in thin films due to the restricted geometry. The bandgap estimated here of ~0.6 eV is on the lower side of expected bandgap range. This smaller value could be due to the large Urbach parameter.

Doing a temperature dependence and a film thickness dependence on the Urbach parameter would provide much more insight into the disorder on the electronic structure.

FIGURE 3.6 Absorption of NbO_2 grown at 1 mTorr and Nb_2O_5 grown at 20 mTorr.

Infrared reflectance measurements were taken of a pure phase CuFeO_2 film with 21 nm thickness, to ensure the correct phase and determine the bandgap (Figure 3.7). The same instrumentation as that used for NbO_2 films was used here. The reflectance of Figure 3.7 shows a slow increase with increasing photon energy. The inset displays the first derivative of the reflectance with respect to the photon energy. At 1.15 eV, there is a sharp increase in the slope (indicated by red fit lines). This suggests the onset of a band edge. CuFeO_2 is known to have an indirect bandgap at 1.15 eV.^{35,72,77}

FIGURE 3.7 Infrared reflectance measurements of delafossite film. Figure taken from Joshi *et al.*⁷²

3.5 Using Fourier Transform Infrared Spectroscopy to Characterize Molecular Vibrations in $\text{YVO}_4\text{:Eu}^{3+}$

An “Infinity Gold” spectrometer by Mattson Instruments was used in transmission geometry to measure molecular vibrations using Fourier Transform Infrared (FTIR) spectroscopy of $\text{YVO}_4\text{:Eu}^{3+}$ NPs (Figure 3.8). The first significant spectral features to point out are the peak and shoulder at 809 cm^{-1} and 920 cm^{-1} , respectively. These are assigned to the V-O bonds of the VO_4 group.⁹¹ The weaker peak located at 452 cm^{-1} , is assigned to the Y-O and Eu-O bonds.⁹¹ Not only is it important to recognize the bonds from within the known crystal structure, the surface chemical composition must also be understood so differences can be compared when the surface is modified, for example when organic ligands are attached to the

surface. Water is commonly absorbed which can be seen with broad band feature centered at 3400 cm^{-1} and the sharp peak at 1650 cm^{-1} .⁹² The broad feature is due to the H-O-H stretch vibrational mode,⁹³ which is broadened due to the ladder of unresolvable, closely spaced, modes that are modified by the surface interactions. The sharp feature is due to H-O-H bending modes. With the chemical synthesis, remnants left over can also be seen. The broad shoulder between 1200 cm^{-1} and 1060 cm^{-1} is associated with POO^- impurity from the use of diphosphonic acid.⁹² Similarly, the peaks near 1373 cm^{-1} and 1517 cm^{-1} are remaining NO_3^- surface groups from the use of HNO_3 .⁹⁴

FIGURE 3.8 Fourier Transform Infrared Spectroscopy of $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles.

3.6 Using Fourier Transform Infrared Spectroscopy to Ensure Organic Ligand Attachment to $\text{YVO}_4\text{:Eu}^{3+}$

With the attachment of organic ligands (NCBA, DHBA and BA) to the surface of the nanoparticles, alterations to chemical composition of the surface should be observed. First, it is important to notice that the main bonds of YVO_4 are unaltered, as can be seen in Figure 3.9. The peaks due to V-O and Y-O bonds are unaltered, indicating the basic crystal structure is not modified. This is expected because the new functional groups are simply attached to the outer surface of the NPs. Figure 3.9 (b) shows the IR spectra within the range of 1000 cm^{-1} to 2000 cm^{-1} , where the majority of the surface modifications are noticed. All of the organic ligands contain aromatic rings, therefore it is no surprise to see the new peaks at 1600 cm^{-1} and 1420 cm^{-1} . These peaks can be assigned to the stretching mode of the aromatic ring.⁹⁵ For the NCBA treatment, there is a peak observed at 1360 cm^{-1} , which can be assigned to the N-O bond. Another indication that the surface molecules of the NPs are replaced by the newly introduced organic ligands is the suppression of the 3400 cm^{-1} and 1650 cm^{-1} features (see Figure 3.9 (a)). It was previously pointed out that these correspond to the H-O-H and adsorbed H_2O respectively. In particular for the DHBA treatment, the presence of a new band at 3600 cm^{-1} is characteristic of free OH.⁹⁶

FIGURE 3.9 Fourier transform infrared spectra of YVO₄:Eu³⁺ nanoparticles and YVO₄:Eu³⁺ with attached aromatic linker molecules benzoic acid (BA), 3-nitro-4-chlorobenzoic acid (NCBA) and 3,4-dihydroxybenzoic acid (DHBA) for the wavelength ranges (a) 4000 – 400 cm⁻¹ and (b) 2000 – 1000 cm⁻¹. Spectra are vertically offset for clarity. Figure from Senty *et al.*⁶⁹

3.7 Using Tauc Plot to Determine Bandgaps

In a parabolic band structure, the linear absorption coefficient, α , is related to the photon energy ($\hbar\omega$) by

$$\alpha \propto (\hbar\omega - E_g)^2 \quad (3.4)$$

Here, E_g is the bandgap and n defines whether the bandgap is direct ($n = 1/2$) or indirect ($n = 2$).

^{74,97,98} Therefore by plotting equation 3.4 in terms of $\hbar\omega$ as

$$(\hbar\omega)^{1/n} \propto \hbar\omega - E_g \quad (3.5)$$

linear regions define the band. These plots are known as Tauc plots.

3.7.1 Tauc Plot on NbO₂ Film

Figure 3.10 demonstrates a Tauc plot of an NbO₂ film grown at 1 m-Torr pressure. When plotted with $n = 1/2$, the data appears very exponential like, as is clearly seen with the red line.

FIGURE 3.10 Tauc Plot of NbO₂ thin film grown at 100 m-Torr, for both $n = 2$ (black, left axis) and $n = 1/2$ (red, right axis). Image modified from Joshi *et al.*⁷⁴

Although when $n = 2$, there is a linear region, indicating that the bandgap is indirect. The linear region can be extrapolated to the axis and from this, the bandgap can be inferred. Here a value of 0.57 eV is obtained, well within previous literature reports of 0.5 to 1.0 eV.^{83–86}

3.7.2 Tauc Plot on Delafossite Powders

Delafossite powders were plotted as Tauc plots for direct (Figure 3.11 (a)) and indirect (Figure 3.11 (b)) bandgaps. At 0% Fe concentration, CuGaO₂ appears to be more linear in the direct bandgap Tauc plot. A line extrapolated to the axis gives a bandgap of 2.8 eV, within the range of previously reported values.^{28,35,99} Figure 3.11 (b) shows that at 100% Fe concentration, CuFeO₂ has a linear region which gives an indirect bandgap of 0.8 eV, within the expected value. At a concentration of 5% Fe, again the bandgap appears to be direct. The Tauc plot gives a value of 1.7 eV. There is little difference in the bandgap of 5% Fe compared to lower concentrations.

FIGURE 3.11 Tauc plots of delafossite powders with Fe concentrations at 0%, 1%, 3%, 4%, 5% and 100% for (a) direct and (b) indirect bandgaps.

3.8 Chapter Summary

UV/vis absorption of CdSe QDs gave a first exciton peak at 2.03 eV. Measurement of CdSe/TiO₂ heterostructure samples gave the same exciton peak. Bandgap measurements of CuGaO₂ and CuFeO₂ delafossites using absorption and Tauc Plots provided bandgap values of 2.8 eV and 0.8-1.1 eV, respectively. It was demonstrated that Tauc plots provide a tool to determining the bandgaps of materials and aid in distinguishing between direct and indirect gaps. The bandgap of NbO₂ thin films were also measured giving an indirect bandgap value of 0.57 eV. Analyzing the Urbach parameter on NbO₂ found a value of 0.2 eV, indicating the existence of impurities within the sample.

A more in depth study shows that doping CuGaO₂ with Fe, breaks the symmetry allowing for lower energy optical transitions to occur. This is due to the preferred Fe doping positions within the crystal lattice. Fe prefers to be at sites which minimize strain on the system. As a consequence, at low concentrations, Fe atoms position themselves within the same crystallographic plane. At a doping level of 5% Fe, there are enough Fe atoms that Fe-Fe distance cannot be maximized within the same plane. Fe atoms begin to position themselves in separate planes resulting in a global strain across the system. Due to the Laporte selection rules, adding Fe into the system allows for a previously forbidden optical transition to now be accessible. This causes the absorption edge to shift to lower energies, decreasing the bandgap.

FTIR measurements confirmed attachment of BA, NCBA and DHBA to the surface of YVO₄:Eu³⁺ NPs by providing signature peaks associated with each ligand. In particular, DHBA showed an extra O-H signature at 3600 cm⁻¹. These results display strong evidence of successful

replacement of molecules absorbed on the NP surface and attachment of the three aromatic linker molecules, with no modifications of the $\text{YVO}_4\text{:Eu}^{3+}$ NPs themselves.

Chapter 4: Photoluminescence and Photoluminescence Excitation

4.1 Introduction to Luminescence

Luminescence occurs when a material releases an excess amount of energy through the emission of light. There are different types of luminescence which are defined by their mode of excitation. When matter is excited with light, it is known as photoluminescence (PL). More specifically, when a photon is incident on a material which has energy greater than the bandgap, the photon will be absorbed. This causes an electron to move from the ground state into an excited state. Upon relaxation of the electron back to the ground state, luminescence or the emission of light is produced. The amount of time the electron spends in the excited states defines whether the luminescence process is fluorescence or phosphorescence. Fluorescence has a lifetime near 10^{-9} - 10^{-7} sec, therefore emission ceases very quickly after excitation has stopped. With fluorescence, relaxation to the ground state occurs by spontaneous emission. Phosphorescence on the other hand has a much longer lifetime than fluorescence and can continue to luminesce even after the excitation radiation has been terminated. Phosphorescence typically occurs on timescales greater than 10^{-3} sec. With phosphorescence, a metastable state exists, temporarily trapping the electron from decaying back to the ground state. A small amount of energy is needed to promote the electron back into the excited state so that a transition to the ground state can occur. The luminescence discussed within this chapter is fluorescence.

With PL spectroscopy, three types of spectra can be obtained to understand light-matter interactions: excitation, emission and time-resolved spectra. For excitation and emission spectra, PL spectroscopy detects and records the dispersion of luminescence radiation into a spectrum which can then be used to understand the electronic structure and emission mechanisms of

materials. To obtain emission spectra, an excitation wavelength which corresponds to energy at or above the bandgap is sent incident onto a sample, and the PL across all wavelengths is collected in a spectrometer. This displays which energy levels are accessed given a specific excitation energy. Following excitation, the electron can transition back to the ground state with a radiative or non-radiative transition. A radiative transition occurs when the excess energy is emitted by a luminescent photon, while non-radiative transitions do not involve emission of a photon but can include energy lost as heat to the crystal lattice. With PL spectroscopy, only radiative transitions are detected.

Excitation spectra or photoluminescence excitation (PLE) spectra are obtained by measuring the luminescence intensity at a specific wavelength, as the excitation wavelength is varied. This technique gives insight into what excitation regions will produce the greatest luminescent intensity and the spectra typically corresponds to the absorption profile.

Time-resolved fluorescence (TRF) spectroscopy utilized time-correlated single photon counting (TCSPC) to measure the time dependent luminescence intensity or the fluorescence lifetime. TCSPC uses periodic excitation to collect the emission intensity over several excitation/emission cycles. It takes an average of the time between the first photon created from the sample relative to the pulse excitation over all of the excitation/emission cycles. From this, an exponential decay of the fluorescent lifetime is created.

4.2 Experimental Technique

A double-monochromated Horiba Jobin Yvon Fluorolog-3-11-TCSPC spectrofluorometer was used in reflection geometry for both PL and PLE measurements. All measurements were

performed in ambient conditions. An excitation wavelength of 400 nm was used for CdSe/TiO₂ heterostructures and 250 nm for YVO₄:Eu³⁺ NPs. For PLE measurements on YVO₄:Eu³⁺ samples, the excitation wavelength was varied, while monitoring various emission peaks captured in the PL spectra. TRF measurements were taken of the C-CdSe QDs using the same instrument, in TCSPC mode. A pulsed excitation source with wavelength of 400 nm and 1 ns FWHM was used and the emission was detected at the exciton peak of 620 nm.

4.3 Effect of Capping Ligands on CdSe/TiO₂ Heterostructure Surface States

The strong fluorescence signal for C-CdSe QDs is displayed in Figure 4.1. The maximum signal strength occurring at 2.0 eV (620 nm) corresponds to the first exciton peak seen in the linear absorption measurements of Chapter 3. Fluorescence measurements were also taken of the UC-CdSe QD, C-CdSe/TiO₂ and UC-CdSe/TiO₂ although the signal was quenched therefore is not displayed here.

FIGURE 4.1 Fluorescence of C-CdSe QDs. Figure modified from Senty *et al.*⁶¹

Capping ligands are placed on the surface of QDs to help maintain a strong fluorescence. For CdSe QDs, the capping ligands are known to bind to the cadmium within the QD, passivating the surface, although selenium is allowed to oxidize.¹⁰⁰ Upon removal of the capping ligands via a hydrazine treatment, the surface of cadmium is no longer passivated, allowing it to oxidize as well.¹⁰¹ A passivated surface reduces the formation of trap states which can increase non-radiative relaxation and decrease efficient luminescence from the exciton.¹⁰² Since the fluorescence was quenched for the UC-CdSe QDs, this suggests there is an increase in the surface trap density once the capping ligands are removed, preventing efficient luminescence. The fluorescence was also quenched for both heterostructures. As discussed in Chapter 3 there was no change in the linear absorption between the UC samples, although as can be seen here, the fluorescence has diminished when comparing QDs. This suggests that traps are quenching the fluorescence in the QDs. A quenched fluorescence can also be an indicator of enhanced charge separation which can explain why C-CdSe/TiO₂ also displayed no fluorescence. Charge separation can also further quench UC-CdSe/TiO₂ heterostructures and will be further discussed in Chapter 5.

TRF taken with a 110 ps time resolution, at an emission of 620 nm gives the radiative lifetime of the excited exciton in the 5.0 nm sized C-CdSe QDs. The fluorescence decay (Figure 4.2) was

fit to a multi-exponential function of the form: $I(t) = \sum_i A_i e^{-t/\tau_i}$, where A_i are the amplitudes and τ_i are the fluorescence lifetimes. From the extracted fit parameters displayed in Table 4.1,

FIGURE 4.2 Time-resolved fluorescence of CdSe QDs (black-solid) and multi-exponential fit from parameters in Table 4.1 (red-dotted). Figure modified from Senty *et al.*⁶¹

the radiative lifetime was measured to be 4 ns. The fit was done by de-convoluting the excitation pulse from the decay and the radiative lifetime was calculated with the intensity average (τ_{avg})

$$\frac{\sum_i B_i \tau_i^2}{\sum_i B_i \tau_i}$$

of the time and amplitude parameters $i = 1-3$. Parameter 4 was disregarded due to the large value of τ_4 being outside of the expected radiative lifetime range and the amplitude (B_4) being significantly smaller than the other parameter's amplitudes.

TABLE 4.1 Time-resolved Fluorescence Fit Parameters

	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)	B_1	B_2	B_3	B_4
CdSe	3400	15.000	540	87.000	2.8E-02	3.4E-03	0.27	2.1E-04

4.4 Photoluminescence for Understanding Electronic States of $\text{YVO}_4\text{:Eu}^{3+}$ Nanoparticles

For lanthanide ions like Eu, the 4f electrons are shielded by the outer shell 5s and 6p electrons. This shielding provides for a strong, long-lived and stable emission. Lanthanides are not good absorbers but doping UV absorbers like YVO_4 with Eu^{3+} ions creates a stable, red emitting, UV light harvester. Figure 4.3 shows a partial energy level diagram of VO_4^{3-} and Eu^{3+} , showing the energy transfer between the two ions. Upon excitation by UV light, photons are absorbed by the VO_4^{3-} host, followed by a thermally activated energy migration process through the vanadate sublattice.¹⁰³ Several energy transfer mechanisms are then possible to either quench or provide radiative emission. Radiative emission occurs when the excited electron is transferred to a Eu^{3+} ion from an adjacent VO_4^{3-} , before decaying back to an unexcited state. Once an electron is transferred to a Eu^{3+} ion, the electron will decay from the $^5\text{D}_0$ to $^7\text{F}_j$ manifold on the order of 740 μs ,⁶⁶ where the most dominant luminescence comes from the $^5\text{D}_0$ to $^7\text{F}_2$ electric dipole transition. As outlined by Huignard *et al.*⁴⁹ there are several factor that can quench the PL. If the Eu^{3+} doping concentration is too low, the excited state will not reach the Eu^{3+} ion and will eventually decay non-radiatively. If the doping concentration is too high, concentration quenching will occur. Surface quenching takes place due to the coordination of atoms at the surface being different than those inside the material, causing traps and non-radiative decay pathways.¹⁰⁴ The mean free path of the exciton is similar to the size of the nanoparticles therefore the probability of reaching the surface increases compared to bulk materials. As a result, the quantum yield of nanoparticles tends to be lower.

FIGURE 4.3 Energy level diagram of YVO₄:Eu³⁺, showing absorption of UV light in VO₄³⁻, transfer of excited electron to Eu³⁺ and then decay with emission of a photon.

PL and PLE measurements were conducted on YVO₄:Eu³⁺ NPs (Figure 4.4). YVO₄ has a bandgap of 3.5 eV¹⁰⁵ therefore excitation at 250 nm ensures that only the VO₄³⁻ ion is being excited. Absorption within the vanadate host leads to an excited electron population where several energy deactivation processes as discussed above, can then occur. Upon successful energy transfer to a Eu³⁺ ion, a strong red luminescence is produced.¹⁰⁶ The red luminescence along with the other observed PL spectra of Figure 4.4 are due to transitions within the f-electron shell of the Eu³⁺ ion.^{57,107}

FIGURE 4.4 Photoluminescence (PL) and photoluminescence excitation (PLE) spectra for as-grown $\text{YVO}_4:\text{Eu}^{3+}$. PL data was captured for an excited wavelength of 250 nm and PLE data was monitored at each of the labeled transitions. PLE spectra are vertically offset for clarity and normalized to the corresponding PL peaks. Figure from Senty *et al.*⁶⁹

Figure 4.4 shows that the as grown 5% $\text{YVO}_4:\text{Eu}^{3+}$ NPs exhibit the strongest emission between 500 to 700 nm. Confirmation of energy being transferred from the vanadate host to the Eu^{3+} ion is verified by lack of emission at energies which correspond to VO_4^{3-} ion states. The strongest features at 614 nm and 618 nm is a doublet that corresponds to the dominant electric-dipole transition: $^5\text{D}_0 - ^7\text{F}_2$. As stated in Chapter 2, this transition is only allowed because Eu^{3+} sits at a site without inversion symmetry. The $^5\text{D}_0 - ^7\text{F}_2$ transition is highly sensitive to deviations

from inversion symmetry due to selection rules for $\Delta J = \pm 2$. From crystal field theory, it is known that the $^7\text{F}_2$ energy level can be split into four Stark sublevels where two of these sublevels

are electric-dipole allowed transitions and the other two are optically forbidden,⁵¹ forming the observed double peak in the emission. The magnetic-dipole transition $^5D_0 - ^7F_1$ produces a spectral feature at about 593 nm. Magnetic dipole transitions are parity allowed, therefore are not as affected by site symmetry. The transition is dominant when Eu^{3+} occupies a crystal site having inversion symmetry, at which point the electric dipole transition is forbidden.

Fitting the lineshapes of the electric-dipole and magnetic-dipole transitions provide a Gaussian profile, rather than Lorentzian or Voigt lineshapes. Table 4.2 shows the extracted spectral center positions and linewidth at FWHM. Our instrumentation can only measure out to 40 ns and was therefore unable to directly measure the lifetimes of these transitions due to them being on the order of hundreds of μs .^{106,108} Good agreement is found between FWHM values here and those quoted in previous literature, and therefore it is expected for our PL lifetimes to be on the same scale as 740 μs .^{56,57,109,110}

PLE spectra within Figure 4.4 were normalized to the strength of the corresponding PL peaks. This allows the weight of the absorption to be compared between emission peaks. Spectra were recorded for the 697 nm, 650 nm, 619 nm, 614 nm, 608 nm, 593 nm, 586 nm, 559 nm and 537 nm features observed in the PL. The sharp rise in the PLE data for wavelengths shorter than 350 nm corresponds to the 3.5 eV bandgap of YVO_4 . The presence of the strong absorption edge indicates that the vanadate host is in fact absorbing photons prior to transferring them to the Eu^{3+} ions.^{48,92} For the PLE spectra corresponding to the PL spectral features at 537 nm, 559 nm and very slightly at 586 nm, there is an additional lower energy band that extends from the band edge out to 425 nm. Electron paramagnetic resonance spectroscopy determined that this corresponds to a $[\text{V}^{4+}]_{\text{A}}$ defect site¹¹¹ which is attributed to the cause of absorption here.

In this case, the energy is sufficiently low to allow for thermal activation of the lowest energy transition in the 5D_j manifold without non-radiative relaxation within that manifold.¹¹² The 559 nm PL feature is extremely weak, because thermal coupling between the YVO_4 and the Eu^{3+} is only allowed in the vicinity of the defect band that has a low density of states.

TABLE 4.2 Spectral Properties of electric-dipole and magnetic dipole transitions.

Transition	Line Center	Full-Width at Half Maximum			
		YVO ₄ :Eu	NCBA	DHBA	BA
$^5D_0-^7F_2$	614.5nm	34.7cm ⁻¹	33.9cm ⁻¹	30.2cm ⁻¹	33.4cm ⁻¹
	618.4nm	36.6cm ⁻¹	35.5cm ⁻¹	29.9cm ⁻¹	35.5cm ⁻¹
$^5D_0-^7F_1$	591.8nm	26.4cm ⁻¹	24.6cm ⁻¹	23.2cm ⁻¹	25.4cm ⁻¹
	593.1nm	36.3cm ⁻¹	34.5cm ⁻¹	25.4cm ⁻¹	31.5cm ⁻¹

4.5 Effects of Photoluminescence on YVO₄:Eu³⁺ with Organic Ligands

Figure 4.5 provides a comparison of the PL spectra before and after attaching the NCBA, DHBA and BA organic ligands to the NPs. Comparison between as-grown and treated YVO₄:Eu³⁺ NPs displays that the general shape of the spectra and spectral positions are unchanged. This confirms that absorption into and transfer from the vanadate host to the Eu^{3+} ion is still taking place after all treatments. The linewidth at FWHM for the treated NPs are also shown in Table 4.2 for comparison to the as-grown NPs. It is clear that the peak positions are unchanged for all treatments and the linewidths at FWHM do not change significantly for the NCBA and BA treatments, but there is a slight trend of a smaller linewidth for the DHBA treatment.

FIGURE 4.5 Emission spectra of as-grown and treated YVO₄:Eu³⁺ nanoparticles excited at 250 nm. The attached aromatic molecules are benzoic acid (BA), 3-nitro-4-chlorobenzoic acid (NCBA) and 3,4-dihydroxybenzoic acid (DHBA). Spectra are vertically offset for clarity.

Figure modified from Senty *et al.*⁶⁹

A ratio of the intensities of the $^5D_0-^7F_2$ electric-dipole transition and $^5D_0-^7F_1$ magnetic-dipole transition provides a more detailed investigation of the electromagnetic environment of the Eu³⁺ ion. The magnetic-dipole transition will dominate when the Eu³⁺ ion is centrosymmetric within the lattice. Any asymmetry with the Eu³⁺ ion's position will make the electric dipole more dominate.^{113,114} For all samples here, the electric-dipole transition dominates, indicating that the Eu³⁺ ion sits at a non-inversion symmetry site. Moreover, comparing the ratio of the $^5D_0-^7F_1$ and $^5D_0-^7F_2$ transition intensities gives a measure of the amount of distortion¹¹⁵⁻¹¹⁷ from the as-grown YVO₄:Eu³⁺ NPs by the treatments. The intensity ratios are 0.2050, 0.1961, 0.220 and 0.2048

(with error of ± 0.0006) for the as-grown $\text{YVO}_4:\text{Eu}^{3+}$, NCBA-, DHBA- and BA-treated NPs respectively. Hence, no significant distortion is present, as might be expected. This also agrees with the FTIR results discussed in Chapter 3, confirming that only surface chemistry is affected by the treatments.

The primary difference when comparing the as-grown samples to those with ligands attached is the overall emission strength. Across all samples, the spectral density and weights are nearly identical. The most notable difference is the suppression of PL emission for the DHBA-treated sample. Considering the spectra have been calibrated to account for differences in molecular surface coverage and NP concentrations, the uniform quenching of the PL is therefore an indication of an additional non-radiative pathway from the Eu^{3+} ions. Hydroxyl groups are known to quench the luminescence from the Eu^{3+} ions,^{118,119} due to the high-frequency O-H vibrational modes coupling with the f-electronic states of the Eu^{3+} ion. The strongest quenching occurs when the radiative transition of the lanthanide dopant is close in energy to an integer number of O-H vibrational quanta and when the quantum number (ν) is smallest.¹²⁰ In the case of Eu^{3+} ions, the energy matching is very close to the quantum number $\nu = 4$, leading to rapid non-radiative relaxation through the hydroxyl groups. This energy transfer and quenching is depicted in Figure 4.6. When observing the FTIR spectra in Chapter 3, there is an extra shoulder at 3600 cm^{-1} , corresponding to the free O-H groups in the DHBA-treated sample. These modes are not observed in the spectra of the other samples (Figure 3.8) suggesting the quenching of the DHBA-treated sample is due to the presence of extra O-H groups.

FIGURE 4.6 Energy diagram alignment of YVO₄:Eu³⁺ with O-H vibrational modes.

Figure 4.7 shows the PLE spectra for (a) the magnetic-dipole transition $5D_0$ - $7F_1$ and (b) the electric-dipole transition $5D_0$ - $7F_2$ for all four NP samples. The data are all normalized to the emission peaks at (a) 593 nm and (b) 619 nm respectively, which provide a comparison of the excitation strengths. For wavelengths shorter than 350 nm, there is a clear indication of absorption into the excited states of the VO₄³⁻ ions, as was seen in Figure 4.4 for the as-grown YVO₄:Eu³⁺. For all samples, the absorption appears to be nearly the same. Considering the absorption is the same across all samples, yet DHBA-treated sample has PL suppression, confirms that the suppression is due to relaxation in the O-H vibrational ladder and not reduced absorption in the vanadate host.

FIGURE 4.7 Photoluminescence excitation spectra for as-grown and treated $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles for the (a) magnetic-dipole $^5\text{D}_0\text{-}^7\text{F}_1$ transition at 593 nm and (b) electric-dipole $^5\text{D}_0\text{-}^7\text{F}_2$ transition at 619 nm. Spectra are normalized to the peak emission at the respective wavelengths and offset for clarity. Figure modified from Senty et al.⁶⁹

The DHBA-treated sample has a slight increase in the relative contribution of the absorption into the $[\text{V}^{4+}]_{\text{A}}$ defect band (Figure 4.7 (a)), as coupling to the Eu^{3+} ions is less affected by the relaxation pathway introduced by the O-H vibration ladder. The PLE spectra also show direct excitation of the Eu^{3+} ions, which is strongest in the as-grown nanoparticles. There is some suppression in the BA- and NCBA-treated NP samples and the strongest suppression is seen in the DHBA-treated NPs. This further indicates the suppression of the effectiveness of the Eu^{3+} ions in the presence of the hydroxyl groups.

4.6 Chapter Summary

It was shown that C-CdSe QDs display a strong fluorescence signal with a radiative lifetime of 4 ns. UC-CdSe, UC-CdSe/ TiO_2 and C-CdSe/ TiO_2 samples have no fluorescence. It was

discussed that strong fluorescence is maintained only when the capping ligands are attached to the QDs due to the capping ligands passivating the QD surface. Upon removal of the capping ligands, surface traps form, quenching fluorescence. Electron transfer also suppresses fluorescence which explains the lack of fluorescence for the two heterostructures.

PL and PLE studies on $\text{YVO}_4:\text{Eu}^{3+}$ NPs demonstrate that aromatic linker molecules can be added as a precursor to functionalization, as long as there are no hydroxyl groups present. Linker molecules without hydroxyl groups do not change the photo-physics of the NPs. It was found that linker molecules containing hydroxyl groups suppress the luminescence. This suppression is due to the O-H vibrational ladder coupling with the radiative relaxation pathway, preventing electron transfer from the vanadate host to the lanthanide ion. Further studies would include attaching biotin and DNA to the linker molecules and determining the effects on PL. For functional molecules containing hydroxyl groups, a dependence on the distance between the Eu^{3+} emitters and the source of the O-H vibration ladder will have to be performed. Since rare-earth doped vanadate crystals can be used to coat a magnetic core for magneto-luminescence applications, further development on magnetic-core, luminescent shell studies need to take place. Nevertheless, it is determined that $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles are suitable for functionalization in nanoscale biomedical applications, where luminescence is important for the application.

Chapter 5: Transient Absorption Spectroscopy

5.1 A Brief Introduction to Nonlinear Optics

Presented here is a brief discussion of some basic nonlinear optics effects and terms. Throughout Chapter 5, several of these nonlinear effects are used within the experimental setup therefore a brief discussion of their origin is required.

Nonlinear optics studies the interaction of light with matter in the regime where the optical properties of the material are modified nonlinearly to the strength of the optical field. When an electric field is incident on a material, the electrons in the material will be displaced, causing a polarization. In linear optics, the induced polarization depends linearly on the strength of the electric field

$$P(\omega) = \epsilon_0 \chi^{(1)} E(\omega) \quad (5.1)$$

where the linear susceptibility ($\chi^{(1)}$) and the permittivity of free space (ϵ_0) are constant. When the displacement becomes large, nonlinear effects will occur. These nonlinear effects are weak therefore the polarization can be expressed as a Taylor series expansion

$$P(\omega) = \epsilon_0 (\chi^{(1)} E(\omega) + \chi^{(2)} E^2(\omega) + \chi^{(3)} E^3(\omega) + \dots) \quad (5.2)$$

where the quantities $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order nonlinear susceptibilities, respectively. Second order nonlinear optical interactions will only occur in crystals which do not

display inversion symmetry, while third order nonlinear interactions will occur in both centrosymmetric and noncentrosymmetric crystals. Second harmonic generation (SHG) or

frequency doubling, sum-frequency generation (SFG), difference frequency generation (DFG) or optical parametric amplification and optical rectification (OR) are all second-order, nonlinear effects which when the second order polarization is expanded, each expression can represent a specific nonlinear mixing process.

$$\begin{aligned}
 P^{(2)}_1 = \epsilon_0 \chi^{(2)}_{12} &+ \chi^{(2)}_{23} \cos[(\omega_2 + \omega_3)z - (\phi_2 + \phi_3) + \phi] \\
 &+ \chi^{(2)}_{32} \cos[(\omega_3 + \omega_2)z - (\phi_3 + \phi_2) + \phi] \\
 &+ \chi^{(2)}_{22} \cos[2(\omega_2 z - \phi_2 + \phi)] \\
 &+ \chi^{(2)}_{33} \cos[2(\omega_3 z - \phi_3 + \phi)] \\
 &+ \chi^{(2)}_{23} \cos[(\omega_2 - \omega_3)z - (\phi_2 - \phi_3) + (\phi_2 - \phi_3)] \\
 &+ \chi^{(2)}_{32} \cos[(\omega_3 - \omega_2)z - (\phi_3 - \phi_2) + (\phi_3 - \phi_2)] \\
 &+ \chi^{(2)}_{11} \cos[\omega_1 z - \phi_1]
 \end{aligned} \quad (5.3)$$

Equation 5.3 displays components which oscillate at different frequencies. The first two expressions of Equation 5.3 represent SHG and lead to the generation of radiation at another frequency. Photons with the same frequency interact with a nonlinear material to generate new photons with twice the frequency. This process is depicted in Figure 5.1 (a). SFG, represented by the third term in Equation 5.3, is similar to SHG, except with SFG, the two input frequencies are different (Figure 5.1 (b)). It is necessary that energy is conserved therefore just like with SHG

where $\omega_1 = 2\omega_2$ or $\omega_1 = 2\omega_3$, SFG requires that $\omega_1 = \omega_2 + \omega_3$. The fourth term in Equation 5.3 represents DFG (Figure 5.1 (d)). From conservation of energy, $\omega_1 = \omega_2 - \omega_3$.

Here, the higher input frequency (ω_2) is destroyed while the lower input frequency (ω_3) is created, amplifying the field. The fifth term in Equation 5.3 represents OR (Figure 5.1 (c)). It can be noted that this term does not oscillate in time as the other terms do. As a result, OR converts oscillating polarization into a static DC polarization. From Equation 5.3, it can also be

pointed out that at each position z within the nonlinear medium, specific phase matching conditions must be met in order for the field to radiate a high intensity. Specifically, for SFG

Equation 5.3 states that not only does $\omega_1 = \omega_2 + \omega_3$ but the phase matching condition requires that $k_1 = k_2 + k_3$. This ensures that the field will interfere constructively and the oscillating second-order polarization will radiate at an angular frequency ω_1 .

FIGURE 5.1 Energy-level diagram of (a) second-harmonic generation, (b) sum-frequency generation, (c) optical rectification and (d) difference-frequency generation.

5.2 Introduction to Transient Absorption Spectroscopy

Measuring ultrafast processes requires a time uncertainty which is smaller than the duration

of the process being detected. Photon absorption and emission, several scattering processes,

some chemical reactions and molecular vibrations can occur on timescales as fast as pico- or femtoseconds. Detectors such as fast photodiodes cannot reach the required time resolution therefore alternate techniques such as pump-probe methods have been developed to provide indirect measurements to understand ultrafast light-matter interactions.

Upon photoabsorption, short-lived excited states are accessed which decay back to the ground state through different decay pathways. With ultrafast pump-probe spectroscopy or transient absorption spectroscopy (TAS) the entire absorption and decay process can be studied in real time. In TAS, a short pump pulse on the order of 100 fs promotes a small number of electrons into an excited state. A second, low intensity probe pulse is also incident on the sample which monitors the changes in absorption induced by the pump beam.¹²¹ The probe can be broadband or a single wavelength and the intensity is low enough that no outside processes can be induced. By sending the probe beam through a delay stage, the delay time (τ) between the pump and probe beams can be adjusted (Figure 5.2). For each time step, a differential absorption (ΔA) or transmission (ΔT) is calculated by subtracting the absorption (transmission) spectrum of the ground state from the absorption (transmission) spectrum of the excited state. The differential absorption (transmission) is then normalized by the absorption (transmission) of the ground state to create a normalized transient signal ($\Delta A/A_0$ or $\Delta T/T_0$). By continually taking small time steps between the arrival times of the two beams, the entire decay process can be mapped out in real time.

Although TAS is a four-wave mixing, third order nonlinear technique, it is traditionally not considered nonlinear. Four-wave mixing involves two interactions with two separate pump beams and a probe, while for TAS, a double interaction of the pump pulse and an interaction

with the probe occurs. Due to TAS only involving two physical beams, typically it is simply considered a measurement of absorption of one beam (the pump) by a second beam (the probe).

FIGURE 5.2 Schematic diagram of transient absorption spectroscopy.

A transient signal contains contributions from different processes which when combined, form the full time and wavelength dependent differential transient spectrum. Figure 5.3 shows pictorially why a *bleach* and an *absorption* produce a negative and positive absorption (positive and negative transmission) signal, respectively. During a *bleach*, the pump pulse promotes carriers into an excited state, leaving the ground state with fewer carriers. The absorption of an excited sample is consequently less than the absorption of a non-excited sample, creating a negative differential absorption signal (positive for transmission). Stimulated emission also produces a negative differential absorption signal. For optically allowed transitions, the probe pulse can promote stimulated emission to the ground state, from an already excited sample. The resulting photon is emitted in the same direction as the probe and both photons are detected. There is an increase in the amount of light incident on the detector (positive change in transmission), corresponding to a negative change in absorption. An *absorption* on the other hand will be positive

Bleach

Absorption

FIGURE 5.3 Schematic diagram of sign of transient absorption signal for bleach and absorption. If a semiconductor is probed near the band edge or an absorption band, after excitation with the pump beam, less carriers will be present in the ground state, leading to a decrease in the overall absorption of the probe. This results in a bleach which displays a negative absorption signal. If the probed state is unoccupied before excitation and the excitation wavelength pumps carriers directly into the band, the resulting differential absorption is positive because more light will be absorbed after excitation. Modified from Li *et al.*¹²²

(negative for transmission). Certain wavelengths will allow optical transitions from excited states to higher excited states. These wavelengths will absorb the probe pulse causing fewer photons

to hit the detector, creating an increase in the differential absorption signal (decrease for transmission).^{122,123}

5.3 Experimental Techniques

The TAS experimental setup design allows for a single wavelength pump beam to be used with a single wavelength (tunable between 325 – 2500 nm), broadband visible (440 – 1000 nm) or broadband Terahertz (0.5 – 3 THz) probe. TAS measurements are performed using a Ti:sapphire laser amplifier operating at a central wavelength of 800 nm, 1 kHz repetition rate, an average power of 3.5 Watts and 100 fs pulses. The laser amplifier uses a seed and a pump laser, two diffraction gratings and a Ti:sapphire crystal to generate short, powerful pulses by chirped pulse amplification (CPA). First, a weak but short-duration pulse is generated using a modelocked Ti:sapphire laser, pumped with a green continuous-wave diode laser. The pulse duration is sub-femtosecond at an 80 MHz repetition rate with an average output power of 300 mW at 800 nm. This system serves as the seed laser for the amplifier. After initial ultrashort pulse generation, the beam is sent incident onto a diffraction grating, dispersing the different frequencies. This stretches the pulse duration 10,000 times its original size, significantly reducing the peak power. The power must be reduced so that during amplification, the Ti:sapphire gain medium is not damaged, and nonlinear effects which may cause spatial and temporal pulse reshaping or distortion can be avoided. The next step after stretching the pulse is regenerative amplification. The Ti:sapphire gain medium of the amplifier is initially pumped by a diode-pumped, Q-switched Nd:YLF (neodymium-doped yttrium lithium fluoride) laser, with an operating wavelength of 527 nm with a 1 kHz repetition rate. The repetition rate of the amplifier is 1 kHz while as already discussed, the seed is much faster at 80 MHz. Most of the pulses from

the seed are not amplified, but instead the addition and release of pulses is controlled by manipulating their polarization. For amplification to occur, first a seed pulse (initially with S-polarization) is allowed to enter the regenerative amplifier cavity. Double passing the pulse through a quarter-wave plate causes the polarization to rotate by 90 degrees (now P-polarized). When a voltage is applied to a Pockel cell (a voltage-controlled wave plate), it causes it to act like a quarter-wave plate, therefore a double pass will again rotate the polarization by 90 degrees. After the initial 90 degree rotation from the quarter-wave plate, double passing through the quarter-wave plate and the Pockel cell with an applied voltage, causes no net change to the polarization and the pulse remains P-polarized for multiple round trips while all other seed pulses remain S-polarized. The crystal transmits P-polarized light therefore after multiple passes the pulse is amplified. After about 15 round-trips, a voltage is applied to a second Pockel cell which rotates the amplified pulse back to S-polarization. The pulse is then allowed to leave the amplification cavity. Once amplified, the pulse is then compressed much like it was initially stretched, but reversed. Instead of providing the bluer frequencies with a longer path length as is done with the stretcher, in the compressor, the diffraction grating is positioned so that the bluer frequencies travel the shortest path. This allows them to “catch up” with the redder frequencies, and the result is an ultrashort, amplified pulse.

Output from the laser amplifier is split through a 50/50 beamsplitter, with half the beam used as the input to an optical parametric amplifier (OPA). The OPA produces IR light, with an average power output of 100 – 400 mW, depending on the wavelength. The output consists of two beams; a signal and an idler, allowing tunability between 1120 – 1620 nm and 1620 – 2500 nm, respectively. To generate IR light, the 800 nm input is split so that a small fraction is used

to produce a white-light continuum (WLC) in a sapphire plate. The WLC, used as the seed for DFG, and another fraction of the 800 nm pump are focused non-collinearly, into the pre-amplifier beta barium borate (BBO) crystal. Wavelength tunability is obtained by adjusting, the time delay between the pulses, and the angle of the crystal, to obtain optimal phase-matching conditions. The resulting pump and idler beams are blocked while the signal beam is expanded to be used as the seed for the second amplification stage. The remainder of the 800 nm pump and the signal are overlapped collinearly on a second BBO crystal. Once again, the BBO crystal angle and pump delay are adjusted to tune to the desired signal and idler wavelengths produced through parametric amplification.

Single wavelength probe TAS experiments are conducted on a home built, non-degenerate pump-probe setup (Figure 5.4). The experimental setup was designed so that the pump and probe pulses can be switched between the amplifier and OPA allowing complete flexibility in the range of pump and probe wavelengths (not shown in schematic of Figure 5.4). Using SHG in a BBO crystal, pulses from the amplifier and/or OPA can also be frequency doubled tuning the amplifier to 400 nm and the OPA to visible wavelengths (570 – 700 nm). SHG of the 800 nm amplifier beam is performed in a 14 x 14 x 0.5 mm BBO, cut at an angle of $\theta = 29.2^\circ$. For SHG of the IR beam from the OPA a 5 x 5 x 0.5 mm BBO, cut at an angle of $\theta = 21^\circ$ is used. For visible wavelengths less than 570 nm, a SFG setup is implemented by mixing the amplifier's 800 nm beam with an IR beam from the OPA in the BBO crystal cut at $\theta = 21^\circ$. Near UV regions of the spectrum can also be accessed by using SHG twice. For example, a 1300 nm beam from the OPA can be frequency doubled to 650 nm, then the 650 nm beam can again be frequency doubled to 325 nm in a second 5 x 5 x 0.5 mm BBO crystal cut at $\theta = 36.7^\circ$.

A beam chopper is placed within the pump beam path with its frequency set to that of the laser amplifier. The chopper blocks the pump beam path half the time, allowing for measurement of the probe with and without the pump pulse. The time-delay between the pump and probe pulses is controlled by a motion control system with a 3 ns relative time delay. The single wavelength transmission probe radiation is focused onto the sample, sent through a monochromator, collected on a silicon photodetector and recorded with a lock-in amplifier (Figure 5.4).

FIGURE 5.4 Schematic diagram of pump-probe experimental set-up. BS: beam splitter, BBO: β -Barium Borate non-linear crystal, OPA: Optical Parametric Amplifier.

Tightly focusing the high power, ultrafast pulses provided by the Ti:Sapphire laser amplifier within a transparent media provides a broadening of the pulse's spectrum, leading to a white-light continuum (WLC). A broad range of materials can be used, including sapphire, calcium fluoride, gases, and in our case, cool-flowed water. The water is contained in a 10 x 10 mm cuvette. Tubes attached to each end of the cuvette allow water to flow through the cuvette and into a chiller. This ensures that heating and boiling of the water from the high powered pulses does not disrupt the continuum generation. A 750 mm lens is used to focus the beam within the

water and the output WLC is collimated using a 500 mm concave mirror. A pin is used to block a portion of the intense residual 800 nm light at the center of the WLC. Visible broadband probe radiation is then sent through a 25 x 36 x 1 mm, 90:10 beamsplitter. The 10 % portion of the beam is routed around the sample and into the spectrometer to be used as a reference beam.

FIGURE 5.5 Schematic diagram of pump-probe white light continuum experimental set-up. BS: beam splitter, BBO: β -Barium Borate non-linear crystal, WLC: white light continuum, RB: reference beam, SB: signal beam, CCD: CCD camera.

The 90 % portion of the beam is focused onto the sample with a 1000 mm concave mirror. After the sample, the signal is collimated using a 100 mm achromatic lens, routed into a $\frac{1}{4}$ m spectrometer and collected on a CCD camera. Irises are used to block scattered light and neutral density filters are used to decrease the intensity of the beam so as not to saturate the CCD camera. For data acquisition of WLC spectra, a chopper is not used but instead automated shutters are opened and closed to allow for collection of background, pump-on and pump-off spectra. Background spectra is subtracted from pump-on and pump-off data which are then used to calculate $\Delta T/T$. The delay time between pulses is controlled with a 3 ns time range

motion control system. A simplified schematic diagram of the pump-probe WLC setup is displayed in Figure 5.5.

A schematic diagram of the experimental setup for optical pump, THz probe is shown in Figure 5.6. Ultrashort optical pulses derived from the laser amplifier are used to generate and detect the THz. THz generation (between 0.5-3 THz) occurs through OR by pumping a zinc germanium phosphide (ZGP) crystal with the OPA output tuned to 1200 nm.¹²⁴ The THz pulse is collected, focused onto the sample and recollected for detection, using a four off-axis parabolic mirror setup. Electro-optic (EO) sampling in ZnTe is used to detect the THz pulse. EO sampling compares a gate pulse's polarization state after transmitting through the EO crystal. When the THz field and gate do not overlap, the gate simply passes through the EO crystal unaltered. After passing through a quarter-wave plate and Wollaston prism (a prism which separates randomly polarized or unpolarized light into two orthogonal linearly polarized outgoing beams), the gate is broken into equal intensity, vertically and horizontally polarized waves. A balanced detector will measure no difference in the wave intensity. In the case of a THz field being present, the gate is induced with birefringence, creating a slightly elliptical transmitted beam. The detectors no longer read a completely balanced beam, indicating the presence of the THz field which can be measured when taking the difference of the intensities from the two detectors.

FIGURE 5.6 Schematic diagram of terahertz generation and detection with optical pump.

SFG is used to tune the pump pulses from the amplifier to 400 nm in a BBO crystal with a pump fluence of $\sim 1 \text{ mJ/cm}^2$. The pulses are sent through a delay stage (τ_2) and focused onto the sample to allow for the decay of the peak of the THz probe pulse to be monitored as a function of the probe delay time.

5.4 Terahertz Transient Absorption Spectroscopy on Delafossites

$\text{CuGa}_{1-x}\text{Fe}_x\text{O}_2$ delafossites with Fe concentrations at $x = 0 - 0.5, 1$ were photoexcited with a 400 nm excitation pulse and probed with a broadband THz pulse between 0.5–3 THz¹²⁴ in ambient conditions. The THz delay stage (τ_1 of Figure 5.6) was fixed at the peak of the THz pulse and the 400 nm pump delay was scanned. This type of scan is referred to as a 1D pump scan and provides information about the sample's average THz absorption.¹²⁵ THz TAS relates

the measured differential transient signal ($\Delta\epsilon/\epsilon_0$ or $\Delta T/T_0$) to the mobility or conductivity of

photoexcited electrons.¹²⁵ The Drude Model shows⁴²⁶ that the change in $\Delta\sigma/\sigma$ is proportional to the differential transient: $\Delta\sigma \propto \Delta T$. A change in $\Delta\sigma/\sigma$ can not only be related to the average THz absorption by free carriers, but can also be due to a changing index of refraction or pertain to the transient absorption being frequency dependent. A 1D pump scan loses information about the frequency and phase shifts between the real and imaginary parts of the detected signal. Therefore a 1D pump scan takes a representative slice which is proportional to the magnitude of the complex signal and therefore is only a magnitude of the THz conductivity. To obtain the complete dynamical information about the sample, a full 2D scan in both time and THz frequency is required although a single 1D scan can obtain some knowledge of the dynamics.

The THz decay in Figure 5.7 shows a large signal strength for 0% Fe, which then decreases for 1% Fe. For Fe concentrations greater than 1%, the signal strength slightly decreases again. Due to the similarity in the signal for 2 – 5% Fe concentrations, Figure 5.7 only displays an Fe concentration of 5%. The decrease in signal strength indicates that as soon as Fe is introduced into the system, there is a large decrease in the change in conductivity. This suggests that the charge density for 0% Fe concentration is distributed to allow more mobility, while it limits charge mobility for 1 – 5% Fe concentrations. The charge density distributions across the HOMO for 0 – 5% Fe concentrations were discussed in Section 3.2. It was pointed out that at 0% Fe concentration, the HOMO has an oscillatory charge distribution across the Cu atoms throughout the crystal, while for 1 – 5% Fe concentrations, discrete clusters of charge surrounding the Fe atoms form (Figure 3.4). For Fe concentrations greater than 0%, these

discrete regions decrease the charge mobility across the crystal structure within the HOMO creating the lower THz TAS signal seen in Figure 5.7.

FIGURE 5.7 THz transient absorption for 0%, 1% and 5% Fe concentrations with 400 nm excitation pulse and a THz probe.

5.5 Transient Absorption Spectroscopy on $\text{YVO}_4\text{:Eu}^{3+}$

Figure 5.8 displays normalized TAS measurements of $\text{YVO}_4\text{:Eu}^{3+}$, $\text{YVO}_4\text{:Eu/BA}$, and $\text{YVO}_4\text{:Eu/DHBA}$, taken with a 325 nm pump with 250 μm spot size at 2 mW, and a 800 nm probe with 60 μm spot size at 0.5 mW. Measurements were taken in ambient conditions.

FIGURE 5.8 Normalized transient absorption of $\text{YVO}_4:\text{Eu}^{3+}$ (purple), $\text{YVO}_4:\text{Eu}^{3+}/\text{BA}$ (blue) and $\text{YVO}_4:\text{Eu}^{3+}/\text{DHBA}$ (green) with 325 nm pump, 800 nm probe.

Pumping with 325 nm ensures that only the YVO_4 host is excited. The 800 nm probe mainly looks at free carrier absorption. There is some fluorescence emission of $\text{YVO}_4:\text{Eu}^{3+}$ at 811.9nm, 815.2nm and 817.2nm corresponding to the $^5\text{D}_0\text{-}^7\text{F}_6$ transition, which could be probed here.⁵⁷ Figure 5.8 displays a similarly decaying, long lifetime for all samples as expected, since the PL lifetime is on the order of μs . There is little difference between the pure $\text{YVO}_4:\text{Eu}^{3+}$ and $\text{YVO}_4:\text{Eu}/\text{BA}$, although there is significant difference in the early decay times for $\text{YVO}_4:\text{Eu}/\text{DHBA}$. Each of the decays were fit to multi-exponential function and the time decay constants are displayed in Table 5.1 showing τ_1 and τ_2 are much faster for $\text{YVO}_4:\text{Eu}/\text{DHBA}$ compared to the other two samples.

TABLE 5.1 Decay time constants

	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)
$\text{YVO}_4:\text{Eu}$	21.4	81.2	467.8	170329
$\text{YVO}_4:\text{Eu}/\text{BA}$	24.5	91.9	803.8	217833
$\text{YVO}_4:\text{Eu}/\text{DHBA}$	4.4	35.6	431.3	168710

Considering the initial fast decay is only present when DHBA is attached to the sample, it must be due to the presence of the ligand. DHBA quenches the PL from $\text{YVO}_4:\text{Eu}^{3+}$. Since the electrons are not escaping in the form of radiative relaxation, there could be electron transfer happening between $\text{YVO}_4:\text{Eu}^{3+}$ and DHBA. The electron transfer can be calculated with

$$\frac{1}{\tau_{\text{YVO}_4:\text{Eu}^{3+}}^{\text{DHBA}}} = \frac{1}{\tau_{\text{YVO}_4:\text{Eu}^{3+}}} + \frac{1}{\tau_{\text{YVO}_4:\text{Eu}^{3+}}^{\text{DHBA}}} \quad (5.4)$$

which gives the electron transfer happening between 5.5 – 63 ps.

As will be discussed in the following sections of this chapter, calculation of electron transfer rates using this method is limited within the low excitation regime. There is also a lack of the complete picture of the full dynamics which are occurring. Although it is not discussed on these samples, Section 5.8 develops an alternate method of analyzing transient absorption data, providing a complete carrier dependent lifetime.

5.6 Exponential Modeling of Transients

When modeling transient decays, the following rate equation is often used:

$$\frac{dN}{dt} = -\frac{N}{\tau} = -N \left(\frac{1}{\tau_{\text{SRH}}} + \frac{1}{\tau_{\text{RR}}} + \frac{1}{\tau_{\text{Auger}}} + \dots \right) \quad (5.5)$$

where N is the excited carrier density and τ is the carrier lifetime, which can be broken up into a Shockley-Read-Hall lifetime (τ_{SRH}), a radiative recombination lifetime (τ_{RR}) and an Auger recombination lifetime (τ_{Auger}), as well as additional mechanisms. During Shockley-Read-Hall recombination, also known as trap-assisted recombination, the electron decays through a trap state within the band. Radiative recombination is a form of spontaneous emission where a

photon is emitted which corresponds to the energy of the band the electron is decaying from. Auger recombination is a high carrier density process where the energy is given to a third carrier, which is then excited into a higher energy level. A schematic diagram of these processes is displayed in Figure 5.14 (a).

For low carrier concentrations ($n \gg n_0$, where n_0 is the equilibrium carrier concentration), a single exponential decay solution can be found, assuming that the lifetimes do not depend on the carrier density. Transient decay data can then be fit to an exponential solution and the decay time (τ) extracted. For heterostructure samples, if it is assumed that the only change in kinetic decay between the two materials (for example CdSe/TiO₂) is the addition of electron transfer, the electron transfer rate (k_{ET}) can easily be calculated. In the case of low-level injection and first order kinetics

$$\frac{1}{\tau} = \frac{1}{\tau_{CdSe/TiO_2}} + \frac{1}{\tau_{CdSe}}, \quad (5.6)$$

where τ_{CdSe/TiO_2} and τ_{CdSe} are the decay times extracted from the heterostructure and QD samples respectively. This suggests that the change in lifetime of the donor (QD) is equal to the charge transfer and, assumes no other modifications of the relaxation dynamics occur upon heterostructuring. An issue commonly arises when fitting transient decays to exponential solutions. Mainly the decays rarely fit to a single exponential and must be modified to a sum of multiple exponentials

$$\Delta n(t) = n_1 e^{-t/\tau_1} + n_2 e^{-t/\tau_2} + n_3 e^{-t/\tau_3} + \dots \quad (5.7)$$

—

1

2

3

Analyzing multi-exponential decays, usually results in assigning nanosecond timescales to radiative e - h recombination¹²⁷, although Shockley-Read Hall recombination can also dominate⁷⁴. The faster components are typically attributed to electron-trapping, electron transfer^{128–130} and Auger recombination^{131,132}, ignoring the fact that these higher-order decay processes are dependent on the carrier density, and that the main assumption of this analysis requires being in the low carrier concentration regime where higher-order dynamics do not occur. These assumptions provide error in the analysis because one must choose, (i) the time constants that belong to charge transfer, and (ii) the constants that change as a result of new interfacial recombination channels in the heterostructure.

An alternative approach is to take a time average of the lifetime to find the average difference. This method removes the ambiguous step of defining nonlinear recombination mechanisms to an exponential decay component although, the information about which time scales change upon heterostructuring is also lost. Nevertheless, there are two time average approaches that are commonly used; an amplitude average: $\tau_a = \frac{\sum_i \tau_i}{\sum_i 1}$ and an intensity average: $\tau_i = \frac{\sum_i \tau_i^2}{\sum_i \tau_i}$. Choosing which time average is best to use given a certain sample is proven to be difficultⁱⁱⁱ¹³³ although, the amplitude average better describes a mean lifetime and the intensity average better describes the average time spent in the excited state¹³⁴.

5.7 Using Transient Absorption Spectroscopy to Understand Charge Dynamics in CdSe/TiO₂ Heterostructures

The ultrafast, complex charge dynamics of light harvesting materials can be tracked with TAS. Charge separation, recombination and loss pathways can be mapped out. In heterostructure materials, the success of TAS is particularly seen in QD-TiO₂, where the electron

FIGURE 5.9 Normalized transient absorption decay for CdSe QDs (black), UC-CdSe/TiO₂ (blue) and C-CdSe/TiO₂ (orange). Inset: schematic band diagram for C-CdSe/TiO₂ and UC-CdSe/TiO₂. Figure from Senty *et al.*⁶¹

transfer efficiency has been found to be highly dependent on the chain length of the ligand used to attach the QD to TiO₂. Dibbell and Watson show that electron injection decreases when the chain length increases (the chain links the QD and TiO₂).¹³⁵ The incident photon-to-current efficiency has also been shown to increase when QDs are directly absorbed onto TiO₂ versus using linking molecules, increasing the coverage of TiO₂, so long as the QDs do not aggregate.^{128,136} Decay dynamics are also heavily affected by the size of QDs. Robel *et al.*¹³⁷ and

Zhu *et al.*¹³⁸ show that the electron transfer rate increases for decreasing QD size. The Auger rate has also been shown to rapidly decrease for increasing nanoparticle radius following an r^{-2} dependence.¹³⁹ The presence of surface passivation layers decreases the number of trap states therefore eliminating some nonradiative recombination pathways.^{140,141}

Progress has been made for QD-TiO₂ heterostructures through the careful comparison of lifetimes with systematic variation of the components in the heterostructure, although individual transients recorded from TAS are difficult to analyze on their own. Moreover, the complexity of the dynamics means that assigning recombination mechanisms to various portions of the transient may lead to ambiguous results.

TABLE 5.2 Exponential Decay Fit Parameters:

	A_1	A_2	A_3	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
CdSe	0.205	0.173	0.117	61.4	293	2440
C-CdSe/TiO ₂	0.00544	-	0.0120	53.3	-	601
UC-CdSe/TiO ₂	0.0485	0.0612	0.0721	48.8	227	1540

Single wavelength probe TAS was conducted on CdSe, C-CdSe/TiO₂ and UC-CdSe/TiO₂. The pump and probe pulses from the amplifier and OPA were frequency doubled in a BBO crystal to tune to 3.1 eV (400 nm) and 2.03 eV (610 nm) respectively, and focused to the same spot on the sample with beam sizes of 850 μ m and 200 μ m respectively. Measurements were performed in ambient conditions. Normalized transient absorption decays of the three samples are shown in Figure 5.9. The inset displays schematic band diagrams for each heterostructure, showing the excitation and transfer process. The decays across all samples are very similar, emphasizing the challenge in making meaningful statements about transfer rates. The transient

signal strength for C-CdSe/TiO₂ is much weaker compared to the others and the data was smoothed using an adjacent-average method, for presentation purpose only.

Figure 5.9 highlights that after heterostructuring with and without caps, the initial decay appears unaltered until roughly 50 ps. After 50 ps, the UC-CdSe/TiO₂ decay slows slightly before matching the long lifetime of the CdSe QD after 1500 ps. C-CdSe/TiO₂ follows the same initial behavior as UC-CdSe/TiO₂, but for longer time delay, approaches zero much faster. This behavior suggests that the time window for the electron transfer rate is approximately between 50 to 1500 ps.

TABLE 5.3 Electron transfer rates:

	Short (ps ⁻¹)	Medium (ps ⁻¹)	Long (ps ⁻¹)	Amplitude (ps ⁻¹)	Intensity (ps ⁻¹)
C-CdSe/TiO ₂	0.0025	0.015	0.0013	0.00091	0.0012
UC-CdSe/TiO ₂	0.0042	0.001	0.00024	0.000009	0.00024

The transient decays of CdSe QDs, C-CdSe/TiO₂ and UC-CdSe/TiO₂ from Figure 5.9 were all fit to multi-exponential solutions (equation 5.7), and the resulting fit parameters are in Table 5.2. C-CdSe/TiO₂ heterostructure fit best to a double exponential function while CdSe QD and UC-CdSe/TiO₂ heterostructure fit better to triple exponential functions, with the CdSe QD's long lifetime approaching the 4 ns radiative lifetime (see Section 4.3). The fitting illustrates the difficulty with this approach; one or more data sets must therefore be over or under fit, or a comparison between the short and medium time components of the exponential decays must be performed. Here, a comparison is made between the short and medium components for C-CdSe/TiO₂. Equation 5.6 is used to calculate electron transfer rates for the “short”, “medium” and “long” decay times. These transfer rates are shown in Table 5.3. They all lie within the

expected 10^7 - 10^9 s⁻¹ range.^{129,142–145} The wide range of reported electron transfer rates and ambiguity in assigning time constants makes it difficult to systematically compare changes in charge transfer rates due to the presence or absence of the surface ligands. For comparison, Table 5.3 also displays k_{ET} calculated from the two averaging methods (amplitude and intensity) discussed in Section 5.6.

5.8 Inverting Transients to Understand Concentration Dependent Charge Dynamics

The approach of comparative measurements combined with systematic sample design is not always feasible and it is desirable to understand the charge dynamics from individual transients without additional experiments. Understanding the resulting transient absorption kinetics is difficult because the results are not single exponential decays as is expected from a first-order coupled rate equation. Nonlinear dynamics like Auger recombination, radiative recombination and surface trapping cause the results to stray from simple solutions^{131,146}. To get around this, the experimental decays are usually fit to a sum of exponential functions, and each decay constant is assigned to a different decay mechanism^{135,137}, as described in Section 5.6. This assumes that (i) all lifetimes are independent of the carrier density, which is only true for low carrier injection rates, and (ii) that each component of the exponential sum can be attributed to a single loss, trapping or recombination mechanisms regardless of carrier density. In fact the carrier density decays with increasing delay time between pump and probe pulses, changing the interaction regime from nonlinear dynamics initially to linear dynamics at long times. Moreover, altering the sample design can change the apparent number of exponential components required to fit a transient leading to confusion between assigned decay mechanism and the charge transfer rate (k_{ET}) across the heterostructure interface, which is

often the desired parameter for extraction in TAS. In the QD/TiO₂ system for example, this has led to reported charge transfer rates ranging from 10⁷ to 10⁹ s⁻¹^{129,142–145}. The assignment of time constants to charge transfer and recombination channels discussed in Section 5.6 can be incorrect and is the possible reason for this large disparity in charge transfer times.

Due to the non-exponential nature of kinetic decay dynamics in semiconductors, an issue arises when analyzing the data. The dominating decay mechanisms including Shockley-Read-Hall, radiative, surface recombination and Auger scattering all depend explicitly on the carrier density when outside of low-level injection. For high carrier concentration ($n \ll n_i$) the radiative and Auger lifetimes depend on the carrier concentration:

$$\tau_{SRH} = \frac{1}{\alpha n}, \quad \tau_{rad} = \frac{1}{\beta n}, \quad \tau_{Auger} = \frac{1}{\gamma n^2} \quad (5.8)$$

where α is the Shockley-Read-Hall coefficient (recombination through deep traps), β is the radiative coefficient (which accounts for trap-assisted Auger recombination¹⁴⁷) and γ is the Auger coefficient (which accounts for both the *hh* and *ee* processes). The Shockley-Read-Hall coefficient depends explicitly on n , although it is only dominant at low concentrations therefore α is considered a constant¹⁴⁸. Assigning these definitions allows Equation 5.5 to be written as:

$$\frac{1}{\tau} = \alpha + \beta n + \gamma n^2 + \dots \quad (5.9)$$

where α is the Shockley-Read-Hall coefficient, β is the radiative and trap-state Auger coefficient and γ is the Auger coefficient.

Equation 5.9 cannot be solved explicitly, although if β is assumed to be negligible, it can be reduced to

$$\frac{d^2n}{dt^2} = -\beta n + \alpha n^3 \quad (5.10)$$

Which in turn can be solved to

$$n^2 = \frac{\alpha n_0^2 - 2\alpha}{1 - \alpha n_0^2 - 2\alpha} \quad (5.11)$$

where $n_0 = n(0)/(\beta/\alpha + n(0))$. This analysis method has been used to confirm Auger recombination in semiconductor doped glasses.¹³¹ With this example, it is obvious that if any

higher-order dynamics are present, a solution consisting of a sum of exponentials is not appropriate. Even if the denominator is assumed small and Taylor expanded, the resulting

lifetime in the sum of exponentials will have a relationship based on α , which must be used as

a constraint if fitting to multiple exponents. This method also assumes that β is negligible which as described above, not only defines radiative relaxation, but also contains a term for

trap-assisted Auger recombination.¹⁴⁸ It has been shown that in nanocrystals, trap-assisted

Auger recombination is more dominant than expected and cannot be ignored.^{139,149}

Here, the above described issues are overcome by applying an inversion analysis technique that transforms the transients back into the underlying rate equation without relying on fitting, thus allowing the lifetimes and charge transfer to be extracted unambiguously. This method avoids prejudging the data by assuming an exponential solution, or neglecting terms within the rate equation. To show the potential of this technique, transients of CdSe QDs with and

without capping ligands, heterostructured to TiO₂ are analyzed. The data is *inverted*; converting it back into the underlying rate equation by taking a derivative of the transients^{148,150,151,122}. That is, changing the measured transient from

$$n(t) = \int (k_1 + k_2 n + k_3 n^2 + \dots) n \, dt \quad (5.12)$$

to Equation 5.9. Further, the rate of change of the carrier density obtained by the derivative can be divided by the carrier density to get the instantaneous lifetime:

$$-\frac{1}{n} \frac{dn}{dt} = -\frac{k_1}{n} = \frac{k_1}{n} + \frac{k_2}{n} + \frac{k_3}{n} + \dots \quad (5.13)$$

This step can be applied by smoothing, rather than fitting, the data. It allows the instantaneous lifetime to be plotted against carrier density and direct visualization of the various recombination mechanisms in each carrier density regime. By taking the time derivative of the data, the data itself is taken as the coupled first-order rate equation and avoids fitting the integrated solution of the rate equation, as is done by the conventional methods discussed in Section 5.6. Moreover, the inversion removes any assumptions needed for analyzing the possible recombination mechanisms and their changes with heterostructuring.

To apply inversion analysis, the experimental transient absorption decays are smoothed to remove noise using an impulse response function. In this case, a multi-exponential function is used to simply find a best fit and highly smoothed function for inversion. This does not require any interpretation at this stage and the parameters of the exponential terms and the number of exponential terms have no significance. This is essential for the inversion, because a derivative of the data will be taken, and noise is amplified such that it distorts the time derivative. Hence,

this smoothing process is equivalent to a response function filter that removes very high frequency noise.

Care must be taken when deciding on the number of exponential terms to use for the exponential filter. If too many exponentials are used, the filtering process oversamples the data and can cause extra curvature that is not characteristic of the actual data; see Figure 5.10 (a). Oversampling is usually first evidenced by the amplitudes of the exponentials switching in sign. However, it can also appear as the addition of small amplitude exponentials with time constants much longer than the measurement time scales. This causes the downward curve in Figure 5.10 (a). If too few of exponentials are used, the filtering undersamples the data and will not describe the full dynamics accurately, as seen in Figure 5.9 (b) on short time scales.

FIGURE 5.10 Oversampled, undersampled and well sampled response function filters applied to smooth the transient absorption data as dn/dt (a) and $\Delta T/T$ (b). Figure modified from

Senty *et al.*⁶¹

The autocorrelation of the residuals is helpful in determining the correct number of exponentials to use in filtering the data. Figure 5.11 shows the autocorrelations of the residuals for under, well and oversampled filters with 99% confidence intervals (black dashed) for both data with low and high noise. For the data with low noise, Figure 5.11 (a), the autocorrelation decreases until three exponentials are used. For one and two exponentials, the autocorrelation clearly shows further exponentials are necessary to describe the data. At three exponentials, the autocorrelation falls within the 99% confidence intervals. Use of further filtering does not increase the fit past this point- or the data becomes oversampled. Interpretation is more difficult for noisy data, Figure 5.11 (b), however after the addition of two exponentials the data lies within the 99% confidence intervals and further filtering does not make an improvement on the fit.

FIGURE 5.11 Autocorrelations of the residuals with 99% confidence intervals (CI, black dashed) for both low (a) and high (b) noise data. Figure modified from Senty *et al.*⁶¹

While the autocorrelation of the residuals provides guidelines for the best application of exponential filters (the same practices already used for deriving time decays from exponential

fits) it should still be noted when the inversion analysis is most accurate. Figure 5.12 shows the functional prediction intervals for a noisy data set with a linear time sampling. The data is most accurate for intermediate carrier densities, because at short time scales the small time step relative to the rate of change of the carrier density decreases fitting accuracy, and at long time scales the exponential filter becomes indeterminate - with large changes in time constant not increasing the quality of the fit. These restraints can be overcome by sampling the data logarithmically in time, measuring to longer time scales and carrier densities than the region of interest, and reducing noise in the data through increased averaging. Further, it should be noted that the exponential filter used here is a simple implementation based on the already familiar exponential fitting scheme. This allows previously analyzed data to quickly be inverted. However, the development of more advanced filtering schemes will surely prove beneficial.

FIGURE 5.12 (a) Exponential function (black) and exponential function with noise added (green). (b) Derivative of exponential function along with functional prediction intervals (PI).

Figure modified from Senty *et al.*⁶¹

Once a good response function filter is found, a numerical time derivative of the function is taken. Then by plotting this time derivative in terms of the excited carrier density, a visual plot of the rate equation is displayed. The excited carrier density can be extracted from the transient absorption data with^{122,148,150,151}

$$n = -\frac{1}{\sigma d} \ln \left(1 - \frac{\Delta A}{A} \right) \quad (5.14)$$

where σ is the absorption cross section and d is the sample thickness. The absorption cross section can be extracted by calculating the number of excited carriers at several pump energies

$$n = \frac{I_0 (1 - R)^2 (1 - \exp(-\alpha d))}{\hbar \omega (1 - \exp(-\alpha d))} \approx \frac{I_0 (1 - R)^2}{\hbar \omega} \quad (5.15)$$

where I_0 is the initial pump power in J/cm², α_{pump} is the absorption coefficient in cm⁻¹ at the pump energy, $\hbar \omega$ is the pump energy, R is the reflection coefficient, d is the sample thickness

in cm, and n is still the number of excited carriers/cm³. This can then be compared to the maximum transient absorption signal at the corresponding pump powers

$$\frac{\Delta A}{A} = \sigma n d \approx \sigma n \quad (5.16)$$

By taking the slope of a plot of $\frac{\Delta A}{A}$ vs. $\sigma n = \frac{\Delta A}{A} d$, the absorption cross-section can be found, as displayed in Figure 5.13.

Figure 5.14 demonstrates the inversion analysis and its ability to simplify the understanding of TAS by directly revealing the mechanisms in different excitation regimes, which are illustrated in Figure 5.14 (a). Figure 5.14 (b) shows the rate versus carrier concentration for the

QDs on a log-log plot. The first notable result is that the slope corresponds to the order of the mechanism. Since the carrier density for Shockley-Read-Hall or radiative recombination

go as n , trap-state Auger scattering goes as n^2 , and Auger scattering goes as n^3 , these three regions will have slopes of 1, 2 or 3, respectively and are shown as straight lines on the plot.

FIGURE 5.13 Plot of $\sigma = \frac{\Delta n}{n}$ vs. $\sigma = \frac{\Delta n}{n}$, showing the calculated absorption cross-section.

At high carrier concentrations ($> 4 \times 10^{15} \text{ carriers/cm}^3$), the slope of the plot is 3, confirming that at short time scales, recombination is due to Auger recombination. At medium carrier concentrations (between $1 \times 10^{15} - 4 \times 10^{15} \text{ carriers/cm}^3$), the slope reduces to 2, indicating the recombination is due to trap-state Auger scattering, where a trap state conserves energy and

momentum rather than a third photoexcited carrier. Radiative recombination can be dismissed as responsible for the second order dynamics as the second order relaxation is present with and without capping ligands, even though fluorescence is present and quenched respectively

FIGURE 5.14 (a) Schematic representation of possible recombination mechanisms. (b) Inverted relaxation dynamics of CdSe QDs, displaying the exponential fit of the data in the form of the rate equation. Straight lines display the dominating power regimes corresponding to recombination mechanisms in schematic. Figure modified from Senty *et al.*⁶¹

(Section 4.3). At lower carrier concentrations, ($< 1 \times 10^{15} \text{ carriers/cm}^3$) the steady state lifetime is reached and the slope is equal to 1, corresponding to Shockley-Read-Hall or radiative recombination, depending on whether the time constant matches the measured fluorescence lifetime. If desired, the rate of change of the carrier density can be fit to the corresponding mechanisms to directly get the radiative, trap state and Auger coefficients for each sample as shown in Table 5.4. Alternatively, the difference in carrier density verse instantaneous lifetime

can be directly calculated. This step is simplified greatly from measuring the Auger lifetime by looking at the change in short time scale exponential lifetime verse pump power.

TABLE 5.4 Rate Constants for Linear (α), Quadratic (β) and Cubic (γ) carrier concentration dependencies:

	α (ps ⁻¹)	β (cm ³ ps ⁻¹)	γ (cm ⁶ ps ⁻¹)
CdSe	3.5×10^{-4}	2.2×10^{-20}	1.5×10^{-34}
C-CdSe/TiO ₂	1.7×10^{-3}	1×10^{-20}	1.4×10^{-35}
UC-CdSe/TiO ₂	5.7×10^{-4}	1.8×10^{-21}	3.7×10^{-35}

Figures 5.15 (a) and (b) show τ and $\tau(\diamond)$, respectively. They highlight the differences between heterostructuring with and without capping ligands on the QDs. The sample C-CdSe/TiO₂ shows a much higher τ than CdSe, indicating a slower rate (longer lifetimes). This corresponds to changes in the τ plots, upward shifts indicate faster rates (shorter lifetimes) and downward shifts indicate slower rates (longer lifetimes). Comparing C-CdSe/TiO₂ to CdSe, there is an increase in the long lifetime component from 3.5×10^{-4} ps⁻¹ for the QD to 1.7×10^{-3} ps⁻¹ for C-CdSe/TiO₂. There is also a large decrease in the Auger rate between the two samples (γ in Table 5.4) although the trap state rate (β in Table 5.4) is essentially unaltered, indicating electron transfer starts during the Auger scattering process. Additionally, the crossover to nonlinear recombination from the steady-state region occurs at a higher electron density. The crossover to steady-state becomes more obvious in Figure 5.15 (b) where the lifetime calculated from equation 5.13 is displayed. This result supports a fast one-way electron transfer mechanism at high carrier densities, after which time equilibrium is reached and both forward (from QD to TiO₂) and back transfer are possible. This is consistent with recent measurements on CdS/TiO₂ heterostructures where the donor and acceptor hole

and electron transfer were monitored,¹²² and Auger based electron transfer mechanisms observed.¹³⁸

Comparing the QD to UC-CdSe/TiO₂ in Figure 5.15 (a) reveals that the responses in the steady-state region is only slightly shifted upwards with heterostructuring and the crossover between the nonlinear and steady-state regimes occurs at a slightly higher carrier concentration. In Table 5.4, the trap-state Auger coefficient, β , for QD and C-CdSe/TiO₂ is essentially the same, whereas for UC-CdSe/TiO₂ it is an order of magnitude smaller, suggesting the trap state density and relaxation lifetime have been modified. The steady-state regime extends to higher carrier concentrations for C-CdSe/TiO₂ compared to UC-CdSe/TiO₂. Suggesting that higher-order transfer dynamics are more efficient when the capping ligands are present, suggestive of an Auger-based hopping transfer¹³⁸. When the QDs are uncapped, the presence of the trap states reduces the number of available carriers for transfer to TiO₂ and the carrier concentration must reduce through trap-based Auger¹³⁹ scattering to reach the steady-state regime at a lower carrier concentration.

Figure 5.15 (b) shows the instantaneous lifetimes for the three samples. In all cases the lifetime is shorter at higher carrier densities and it flattens off to the linear lifetime at lower carrier densities. At high carrier density, the heterostructures are dominated by similar nonlinear recombination mechanisms, but at lower concentrations they depart. At low densities C-CdSe/TiO₂ has a lifetime of 600 ps, whereas UC-CdSe/TiO₂ has a much longer lifetime of 1500 ps. UC-CdSe/TiO₂ approaches the QD lifetime, because charge transfer away from the QD is partially suppressed. Since the UC-CdSe/TiO₂ has trap states and given that no fluorescence is observed, the linear lifetime can be assigned to Shockley-Read-Hall

Recombination. Even without fitting and extracting the lifetimes, Figures 5.15 (a) and (b) show how the inverted data can quickly reveal the effects of heterostructuring and ligands on each recombination mechanism.

Although the data presented here simply looks at the dynamics of the donor (QD), by taking TAS measurements which only look at the acceptor (TiO₂) dynamics, a coupled rate equation can then be used to further understand decay pathways between the two materials. This would solidify the existing charge transfer dynamics while also describing the complete decay pathways between both the donor and acceptor. Looking solely in the linear dynamics regime, the coupled rate equations used to describe a donor and acceptor are

$$\frac{dN_{D^+}}{dt} = -\frac{N_{D^+}}{\tau_{D^+}} - \frac{N_{D^+}N_{A^-}}{\tau_{D^+A^-}} \quad 5.17$$

and

$$\frac{dN_{A^-}}{dt} = -\frac{N_{A^-}}{\tau_{A^-}} + \frac{N_{D^+}N_{A^-}}{\tau_{D^+A^-}} \quad 5.18$$

If higher order dynamics are also present, equations 5.17 and 5.18 can be modified to include the higher order terms i.e. Auger recombination or trap-state Auger recombination.

FIGURE 5.16 Lifetime vs. carrier concentration extracted from calculating the amplitude average lifetime of transient decays at several different pump powers. Lines are guides to the eye.

Figure 5.16 displays the lifetime vs. carrier concentration extracted by calculating the lifetime of individual transient decays, each taken at different pump powers. The lifetime of each transient decay was calculated by taking an amplitude average of the time constants extracted from a multi-exponential fit. Figure 5.16 represents the same thing as Figure 5.15 (b) except 14 experiments were required to obtain the data for Figure 5.16 while only 3 experiments (one for each sample) were required for Figure 5.15 (b). Figure 5.16 displays very noisy data and even though it took 14 experiments to obtain these results, it is clear that several more experiments are necessary to provide trustworthy results. The general trends of Figure 5.16 match those of Figure 5.15 (b) although due to the noisy results it is nearly impossible to describe any dynamics occurring only using Figure 5.16. This comparison displays that not

only does the inversion analysis method provide for clearer results, but the reduction in amount of time to obtain data of the same quality is over 30 times faster (assuming it takes 30 experiments to get one carrier concentration dependent plot).

5.9 Comparison of Multi-Exponential and Inversion Analysis

Figure 5.17 compares the magnitude of the transfer rates $|k_{ET}|$ determined by the inversion analysis with those interpreted from exponential decays using the various models described in Section 5.6 and applying equation 5.6. From the inversion analysis, k_{ET} can be determined as a function of carrier concentration. For increasing carrier concentration the transfer rate decreases and becomes negative for concentrations $>1.5 \times 10^{15} \text{ cm}^{-3}$, which corresponds to a slower recombination in the heterostructure than in the QDs alone for this concentration regime.

In contrast, each of the exponential methods provides single k_{ET} values corresponding to each decay component (“short”, “medium” and “long”), amplitude average and intensity average. These values, from Table 5.3, are all positive and plotted as horizontal lines on Figure 5.17. For both heterostructures, the intensity average and long component of the multi-exponential fit are both good estimates of the long time-scale (low carrier concentration) charge transfer and they overlay well on the inversion $|k_{ET}|$. This result is expected because (i) the intensity average reflects the most probable excited state and (ii) the long-lifetimes component are in a region where exponentials are solutions to the rate equation. On short timescales (high carrier concentration), the medium and short components match only the magnitude of the inversion $|k_{ET}|$ in the case of the UC-CdSe/TiO₂ sample, while for the C-CdSe/TiO₂ sample the short and medium components become reversed. Taking an average

of the short and medium transfer rates gives a better estimate of the transfer dynamics in the high carrier regime, because these rates were extracted by comparing a bi-exponential fit for the heterostructure to a tri-exponential fit for the QD. Although the multi-exponential fit gives estimates for the corresponding regions, it does not provide full carrier-concentration dependence or the correct signs for some of the components. The conventional fitting algorithm cannot describe the non-exponential high carrier density dynamics regime, nor can it determine that heterostructuring slows the transfer rate extracted by using equation 5.6.

FIGURE 5.17 Charge transfer rates extracted from the three linear models (traditional: short, medium and long; amplitude and intensity) from Table 5.1, compared to the transfer rate extracted using the carrier dependent lifetimes of Figure 5.15 (b) with equation 5.6 (black). (a) C-CdSe/TiO₂, (b) UC-CdSe/TiO₂. Figure modified from Senty *et al.*⁶¹

5.10 Chapter Summary

As discussed in Section 3.2, when Fe is introduced into the delafossite system, the crystal symmetry is broken, allowing for lower energy optical transitions to occur. The new allowed optical transition is supported with THz TAS measurements suggesting a decreased charge mobility for CuGa_{1-x}Fe_xO₂ when $x \geq 1$. Where previously at 0% Fe, the HOMO displays a

charge distribution across the entire crystal lattice, allowing for easy mobility of charges. Starting at 1% Fe, the HOMO charge distribution is no longer continuous but only contains a single cluster, decreasing the mobility. This clustered charge distribution continues for Fe concentrations of $x \geq 1$.

TAS measurements of $\text{YVO}_4:\text{Eu}^{3+}$ show no difference in decay dynamics when BA is attached to the NPs. Although when DHBA is attached, there is an initial fast decay that occurs. This suggests that DHBA provides a non-radiative relaxation route which quenches the Eu^{3+} ion luminescence as discussed in Chapter 4. Electrons are quickly transferred to the DHBA and decay, preventing efficient luminescence. This electron transfer happens between 5.5 – 63 ps.

Multiple exponential fit models were applied to CdSe/TiO_2 heterostructure systems displaying an electron transfer rate between 10^7 - 10^9 s^{-1} . Inversion analysis has been presented and compared to the multiple exponential fit technique. Inversion analysis can map out the charge carrier dynamics, providing carrier recombination rates and lifetimes as a function of carrier concentration where the multiple exponential fit technique is not dependent on the carrier concentration. The multiple exponential fit technique assumes that each component of the exponential sum describes a single decay mechanism and is only accurate for low carrier injection rates. By inverting individual transients, the relative presence of Auger recombination, radiative recombination, as well as trap-state based mechanisms are found without the necessity of systematic sample variation. The inversion analysis can be achieved without explicitly fitting the data and assuming dynamic mechanisms in various excitation regimes. Furthermore, the analysis is able to unambiguously visualize the recombination mechanism from the slope and the magnitude of the lifetime from the relative position. In the heterostructures presented here, the

charge transfer routes after heterostructuring reveal that charge transfer occurs in conjunction with Auger scattering initially at high carrier densities, followed by a charge equilibration stage at longer time scales. Modifying the surface trap state density by removing the capping ligands modifies the electron transfer efficiency at short time scales and the crossover to steady-state at long time scales. Inversion analysis can provide the instantaneous carrier lifetime without assuming a model and yields k_{ET} as a function of carrier density. Inversion analysis has been compared to conventional multiple exponential fit models, where only the magnitude of the transfer rate is acquired at single averaged carrier densities. The results highlight the power of the inversion analysis technique for extracting charge transfer rates.

Chapter 6: Summary and Conclusion

With the United Nations designating 2015 as the International Year of Light and Light Based Technologies, publishing a dissertation this year on photonic devices cannot be more exciting. By studying light-matter interactions of several multifunctional nanoparticles, this work contributes to providing a broader understanding of the workings in nanomaterials used for photonic devices.

Using various experimental techniques, this work looked at the electron dynamics on CdSe QD, TiO₂ heterostructures, providing knowledge on how capping ligands affect electron dynamics. 5.0 nm sized CdSe QDs were synthesized both with and without MPA capping ligands and attached to TiO₂ NPs. MPA ligands were removed from the heterostructures with a hydrazine treatment for a comparison of electron dynamics between samples with and without capping ligands. With UV/vis linear absorption measurements, the first exciton peak of the QD was found to be at 2.03 eV and the peak did not change between heterostructures. A radiative lifetime of 4 ns was measured for the C-CdSe QDs while the two heterostructures and UC-CdSe QDs had no fluorescence. It was suggested that the lack of fluorescence is due to the capping ligands passivating the QD surface and electron transfer suppressing fluorescence.

Inversion analysis was applied to TA data on CdSe/TiO₂ heterostructures displaying the carrier concentration dependence of carrier recombination and lifetimes. It was discovered that charge transfer and Auger scattering occur initially at high carrier concentrations within the heterostructures. Equilibrium is then reached during the longer time scales. By removing capping ligands the surface trap state density is modified. It was noted that the electron transfer efficiency

is altered to short time scales and the crossover to steady-state at long time scales. Upon comparing inversion analysis with conventional multiple exponential fit models, it was found that multiple exponential fit models only provide the magnitude of the transfer rate which is not dependent on the carrier density. With the use of inversion analysis, a carrier dependent transfer rate can be determined.

Delafossite materials have promising applications in p-type DSSC. Through bandgap engineering, optimal absorption can be achieved. It was found that doping CuGaO_2 with iron, the bandgap of CuGaO_2 is modified. Delafossite powders of $\text{CuGa}_{1-x}\text{Fe}_x\text{O}_2$ were synthesized in a tube furnace at concentrations of $x = 0 - 0.5, 1$. It was found that substitution of Fe into CuGaO_2 , allows for the fundamental gap transition to be accessed. Due to Laporte selection rule, the transition between the HOMO and LUMO is forbidden in CuGaO_2 . Charge density plots of various Fe concentrations show how the parity of the HOMO changes, allowing access to the previously forbidden transition, thereby decreasing the bandgap. This large change in charge density is supported by the huge decrease in charge mobility seen in the THz TA data where the signal significantly decreases at 1% Fe doping. These results support that there is no change in the electronic structure at 5% Fe concentration therefore the large change in absorption seen at a 5% Fe doping level must be due to global strain on the crystal structure from the change in Fe placement within the planes.

Studying the effects of organic ligands on the luminescent effects of $\text{YVO}_4:\text{Eu}^{3+}$ NPs, it was discovered that these NPs are suitable for functionalization in nanoscale biomedical applications. Optical and FTIR studies suggest that aromatic linker molecules can be added as a precursor to functionalizing $\text{YVO}_4:\text{Eu}^{3+}$ NPs, as long as there are no hydroxyl groups present. $\text{YVO}_4:\text{Eu}^{3+}$

NPs were synthesized with a wet chemical synthesis process to be approximately 16 nm in diameter, confirmed by TEM and XRD measurements. Metal-carboxylate coordination allowed for the attachment of three organic linker molecules: benzoic acid, 3-nitro-4-chlorobenzoic acid and 3,4-dihydroxybenzoic acid. FTIR measurements confirm successful attachment of the organic ligands, indicating no modifications to the $\text{YVO}_4\text{:Eu}^{3+}$ NPs. $\text{YVO}_4\text{:Eu}^{3+}/\text{DHBA}$ indicated the presence of an extra O-H signature. Photoluminescence measurements show that linker molecules which contain hydroxyl groups suppress luminescence as seen in $\text{YVO}_4\text{:Eu}^{3+}/\text{DHBA}$. The suppression is due to the O-H vibrational ladder coupling with the radiative relaxation pathway. This prevents electron transfer from the vanadate host to the rare earth ion. TAS measurements indicate similar decay dynamics for $\text{YVO}_4\text{:Eu}^{3+}$ and $\text{YVO}_4\text{:Eu}^{3+}/\text{BA}$ although $\text{YVO}_4\text{:Eu}^{3+}/\text{DHBA}$ displays an initial fast decay before relaxing to similar dynamics seen in pure $\text{YVO}_4\text{:Eu}^{3+}$. This suggests that instead of electrons transferring to the Eu^{3+} ion, they are instead transferring to the DHBA ligand and relaxing non-radiatively through the O-H vibrational ladder. Further development of rare-earth doped vanadate glasses with organic ligands can be accomplished by emerging a magnetic core within the NPs therefore allowing them to be used for magneto-luminescent applications.

Understanding light-matter interactions is vital for the development of the next generation of photonic devices. It allows for the engineering of materials which contain optimal properties. With the use of linear absorption, luminescence, and transient absorption spectroscopies, an understanding of electron transfer, charge mobility and luminescence quenching was found in various nanomaterials.

References

1. Fortunato, E., Barquinha, P. & Martins, R. Oxide Semiconductor Thin-Film Transistors: A Review of Recent Advances. *Adv. Mater.* **24**, 2945–2986 (2012).
2. Omata, T. *et al.* Wurtzite CuGaO₂: A New Direct and Narrow Band Gap Oxide Semiconductor Applicable as a Solar Cell Absorber. *J. Am. Chem. Soc.* **136**, 3378–3381 (2014).
3. Ellmer, K. Past achievements and future challenges in the development of optically transparent electrodes. *Nat. Photonics* **6**, 809–817 (2012).
4. Grills, D. C. & Fujita, E. New Directions for the Photocatalytic Reduction of CO₂: Supramolecular, scCO₂ or Biphasic Ionic Liquid–scCO₂ Systems. *J. Phys. Chem. Lett.* **1**, 2709–2718 (2010).
5. Takeda, H. & Ishitani, O. Development of efficient photocatalytic systems for CO₂ reduction using mononuclear and multinuclear metal complexes based on mechanistic studies. *Coord. Chem. Rev.* **254**, 346–354 (2010).
6. Whipple, D. T. & Kenis, P. J. A. Prospects of CO₂ Utilization via Direct Heterogeneous Electrochemical Reduction. *J. Phys. Chem. Lett.* **1**, 3451–3458 (2010).
7. Hong, J., Zhang, W., Ren, J. & Xu, R. Photocatalytic reduction of CO₂: a brief review on product analysis and systematic methods. *Anal. Methods* **5**, 1086 (2013).
8. Shockley, W. & Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *J. Appl. Phys.* **32**, 510 (1961).
9. Green, M. A. Third generation photovoltaics: Ultra-high conversion efficiency at low cost. *Prog. Photovolt. Res. Appl.* **9**, 123–135 (2001).
10. De Vos, A. Detailed balance limit of the efficiency of tandem solar cells. *J. Phys. Appl. Phys.* **13**, 839 (1980).
11. Li, J. & Wu, N. Semiconductor-based photocatalysts and photoelectrochemical cells for solar fuel generation: a review. *Catal. Sci. Technol.* doi:10.1039/c4cy00974f
12. Inoue, T., Fujishima, A., Konishi, S. & Honda, K. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature* **277**, 637–638 (1979).
13. Mori, K., Yamashita, H. & Anpo, M. Photocatalytic reduction of CO₂ with H₂O on various titanium oxide photocatalysts. *RSC Adv.* **2**, 3165 (2012).
14. Grätzel, M. Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells. *Inorg. Chem.* **44**, 6841–6851 (2005).
15. Kamat, P. V. Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters[†]. *J. Phys. Chem. C* **112**, 18737–18753 (2008).
16. Wang, C., Kwon, K.-W., Odlyzko, M. L., Lee, B. H. & Shim, M. PbSe Nanocrystal/TiO_x Heterostructured Films: A Simple Route to Nanoscale Heterointerfaces and Photocatalysis. *J. Phys. Chem. C* **111**, 11734–11741 (2007).
17. Wang, C., Thompson, R. L., Baltrus, J. & Matranga, C. Visible Light Photoreduction of CO₂ Using CdSe/Pt/TiO₂ Heterostructured Catalysts. *J. Phys. Chem. Lett.* **1**, 48–53 (2010).
18. O'Regan, B. & Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **353**, 737–740 (1991).
19. Nozik, A. J. Quantum dot solar cells. *Phys. E* **14**, 115–120 (2002).

20. Hodes, G. Comparison of Dye- and Semiconductor-Sensitized Porous Nanocrystalline Liquid Junction Solar Cells. *J. Phys. Chem. C* **112**, 17778–17787 (2008).
21. Rühle, S., Shalom, M. & Zaban, A. Quantum-Dot-Sensitized Solar Cells. *ChemPhysChem* **11**, 2290–2304 (2010).
22. Beard, M. C. Multiple Exciton Generation in Semiconductor Quantum Dots. *J. Phys. Chem. Lett.* **2**, 1282–1288 (2011).
23. Semonin, O. E. *et al.* Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell. *Science* **334**, 1530–1533 (2011).
24. He, J., Lindström, H., Hagfeldt, A. & Lindquist, S.-E. Dye-sensitized nanostructured tandem cell-first demonstrated cell with a dye-sensitized photocathode. *Sol. Energy Mater. Sol. Cells* **62**, 265–273 (2000).
25. Choi, H. *et al.* Review paper: Toward highly efficient quantum-dot- and dye-sensitized solar cells. *Curr. Appl. Phys.* **13**, S2–S13 (2013).
26. Nattestad, A. *et al.* Highly efficient photocathodes for dye-sensitized tandem solar cells. *Nat. Mater.* **9**, 31–35 (2010).
27. Mori, S. *et al.* Charge-Transfer Processes in Dye-Sensitized NiO Solar Cells. *J. Phys. Chem. C* **112**, 16134–16139 (2008).
28. Ueda, K. *et al.* Epitaxial growth of transparent p-type conducting CuGaO₂ thin films on sapphire (001) substrates by pulsed laser deposition. *J. Appl. Phys.* **89**, 1790 (2001).
29. Friedel, S. S. *Comptes Rendus Acad. Sci.* **77**, 211 (1873).
30. Pabst, A. Notes on the structure of delafossite. *Am. Mineral.* **31**, 539–546 (1946).
31. Huda, M., Yan, Y., Walsh, A., Wei, S.-H. & Al-Jassim, M. Group-IIIA versus IIIB delafossites: Electronic structure study. *Phys. Rev. B* **80**, (2009).
32. Younsi, M., Saadi, S., Bouguelia, A., Aider, A. & Trari, M. Synthesis and characterization of oxygen-rich delafossite CuYO_{2+x}—Application to H₂-photo production. *Sol. Energy Mater. Sol. Cells* **91**, 1102–1109 (2007).
33. Nie, X., Wei, S.-H. & Zhang, S. B. Bipolar Doping and Band-Gap Anomalies in Delafossite Transparent Conductive Oxides. *Phys. Rev. Lett.* **88**, (2002).
34. Huda, M. N., Yan, Y., Walsh, A., Wei, S.-H. & Al-Jassim, M. M. Symmetry-breaking-induced enhancement of visible light absorption in delafossite alloys. *Appl. Phys. Lett.* **94**, 251907 (2009).
35. Lekse, J. W., Underwood, M. K., Lewis, J. P. & Matraga, C. Synthesis, Characterization, Electronic Structure, and Photocatalytic Behavior of CuGaO₂ and CuGa_{1-x}Fe_xO₂ ($x = 0.05, 0.10, 0.15, 0.20$) Delafossites. *J. Phys. Chem. C* **116**, 1865–1872 (2012).
36. Haycock, B. J., Kylee Rice, M. & Lewis, J. P. High-throughput calculations of alloyed delafossite materials: Application to CuGa_{1-x}Fe_xO₂. *Comput. Mater. Sci.* **86**, 155–164 (2014).
37. Kawano, K., Hong, B. C., Sakamoto, K., Tsuboi, T. & Seo, H. J. Improvement of the conversion efficiency of solar cell by rare earth ion. *Opt. Mater.* **31**, 1353–1356 (2009).
38. Huang, C. K. *et al.* Enhanced light harvesting of Si solar cells via luminescent down-shifting using YVO₄:Bi³⁺, Eu³⁺ nanophosphors: Enhanced light harvesting of Si solar cells using YVO₄ nanophosphors. *Prog. Photovolt. Res. Appl.* **21**, 1507–1513 (2013).
39. Klampaftis, E., Ross, D., McIntosh, K. R. & Richards, B. S. Enhancing the performance of solar cells via luminescent down-shifting of the incident spectrum: A review. *Sol. Energy Mater. Sol. Cells* **93**, 1182–1194 (2009).

40. Kumar, V., Khan, A. F. & Chawla, S. Intense red-emitting multi-rare-earth doped nanoparticles of YVO_4 for spectrum conversion towards improved energy harvesting by solar cells. *J. Phys. Appl. Phys.* **46**, 365101 (2013).
41. Jiang, C., Wang, F., Wu, N. & Liu, X. Up- and Down-Conversion Cubic Zirconia and Hafnia Nanobelts. *Adv. Mater.* **20**, 4826–4829 (2008).
42. Tan, G. L. *et al.* Synthesis and optical characterization of CdTe nanocrystals prepared by ball milling process. *Scr. Mater.* **48**, 1469–1474 (2003).
43. Li, M., Li, R., Li, C. M. & Wu, N. Electrochemical and optical biosensors based on nanomaterials and nanostructures: A Review. *Front. Biosci.* **S3**, 1308–1331 (2011).
44. Corr, S. A., Rakovich, Y. P. & Gun'ko, Y. K. Multifunctional magnetic-fluorescent nanocomposites for biomedical applications. *Nanoscale Res. Lett.* **3**, 87–104 (2008).
45. McDowall, N. B. *et al.* Spectrally tunable magnetic nanoparticles designed for distribution/recollection applications. *J. Appl. Phys.* **107**, 09B327–09B327 (2010).
46. Wang, F., Tan, W. B., Zhang, Y., Fan, X. & Wang, M. Luminescent nanomaterials for biological labelling. *Nanotechnology* **17**, R1 (2006).
47. Riwotzki, K. & Haase, M. Colloidal $\text{YVO}_4\text{:Eu}$ and $\text{YPO}_4\text{:Eu}$ Nanoparticles: Luminescence and Energy Transfer Processes. *J. Phys. Chem. B* **105**, 12709–12713 (2001).
48. Yanhong, L. & Guangyan, H. Synthesis and luminescence properties of nanocrystalline $\text{YVO}_4\text{:Eu}^{3+}$. *J. Solid State Chem.* **178**, 645–649 (2005).
49. Huignard, A., Buissette, V., Franville, A.-C., Gacoin, T. & Boilot, J.-P. Emission Processes in $\text{YVO}_4\text{:Eu}$ Nanoparticles. *J. Phys. Chem. B* **107**, 6754–6759 (2003).
50. Singh, N. S., Ningthoujam, R. S., Luwang, M. N., Singh, S. D. & Vatsa, R. K. Luminescence, lifetime and quantum yield studies of $\text{YVO}_4\text{:Ln}^{3+}$ ($\text{Ln}^{3+} = \text{Dy}^{3+}, \text{Eu}^{3+}$) nanoparticles: Concentration and annealing effects. *Chem. Phys. Lett.* **480**, 237–242 (2009).
51. Jia, G. *et al.* Uniform $\text{YVO}_4\text{:Ln}^{3+}$ ($\text{Ln} = \text{Eu}, \text{Dy}, \text{and Sm}$) nanocrystals: Solvothermal synthesis and luminescence properties. *Opt. Mater.* **31**, 1032–1037 (2009).
52. Pan, G. *et al.* Microstructure and optical properties of Eu^{3+} activated $\text{YV}_{1-x}\text{PxO}_4$ phosphors. *J. Appl. Phys.* **104**, 084910 (2008).
53. Rakov, N., Guimarães, R. B., B, W. L. & Maciel, G. S. Structural and spectroscopic analyses of europium doped yttrium oxyfluoride powders prepared by combustion synthesis. *J. Appl. Phys.* **114**, 043517 (2013).
54. Brites, C. D. S. *et al.* Thermometry at the nanoscale. *Nanoscale* **4**, 4799 (2012).
55. Jaque, D. & Vetrone, F. Luminescence nanothermometry. *Nanoscale* **4**, 4301 (2012).
56. Maksimchuk, P. O. *et al.* Abnormal Low Linewidth Temperature Broadening Observed for $\text{YVO}_4\text{:Eu}$ Nanocrystals. *Ukr. J. Phys.* **57**, 193 (2012).
57. Brecher, C., Samelson, H., Lempicki, A., Riley, R. & Peters, T. Polarized Spectra and Crystal-Field Parameters of Eu^{3+} in YVO_4 . *Phys. Rev.* **155**, 178 (1967).
58. Smith, A. M., Mancini, M. C. & Nie, S. Bioimaging: Second window for in vivo imaging. *Nat. Nanotechnol.* **4**, 710–711 (2009).
59. Weissleder, R. A clearer vision for in vivo imaging. *Nat. Biotechnol.* **19**, 316–316 (2001).
60. Harada, T. & Yoshimura, H. Ferritin protein encapsulated photoluminescent rare earth nanoparticle. *J. Appl. Phys.* **114**, 044309 (2013).
61. Senty, T. R., Cushing, S. K., Wang, C., Matranga, C. & Bristow, A. D. Inverting Transient Absorption Data to Determine Transfer Rates in Quantum Dot– TiO_2 Heterostructures. *J. Phys. Chem. C* **119**, 6337–6343 (2015).

62. Chakoumakos, B. C., Abraham, M. M. & Boatner, L. A. Crystal Structure Refinements of Zircon-Type MVO₄ (M=Sc, Y, Ce, Pr, Nd, Tb, Ho, Er, Tm, Yb, Lu). *J. Solid State Chem.* **109**, 197–202 (1994).
63. Momma, K. & Izumi, F. *VESTA 3* for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **44**, 1272–1276 (2011).
64. Ningthoujam, R. S., Singh, L. R., Sudarsan, V. & Dorendrajit Singh, S. Energy transfer process and optimum emission studies in luminescence of core-shell nanoparticles: YVO₄:Eu–YVO₄ and surface state analysis. *J. Alloys Compd.* **484**, 782–789 (2009).
65. Riwozki, K. & Haase, M. Wet-chemical synthesis of doped colloidal nanoparticles: YVO₄:Ln (Ln= Eu, Sm, Dy). *J. Phys. Chem. B* **102**, 10129–10135 (1998).
66. Riwozki, K. & Haase, M. Colloidal YVO₄:Eu and YP_{0.95}V_{0.05}O₄:Eu Nanoparticles: Luminescence and Energy Transfer Processes. *J. Phys. Chem. B* **105**, 12709–12713 (2001).
67. Van Uitert, L. G. & Iida, S. Quenching Interactions between Rare-Earth Ions. *J. Chem. Phys.* **37**, 986 (1962).
68. Palilla, F. C., Levine, A. K. & Rinkevics, M. Rare Earth Activated Phosphors Based on Yttrium Orthovanadate and Related Compounds. *J. Electrochem. Soc.* **112**, 776–779
69. Senty, T. R. *et al.* Photoluminescence spectroscopy of YVO₄:Eu³⁺ nanoparticles with aromatic linker molecules: A precursor to biomedical functionalization. *J. Appl. Phys.* **115**, 163107 (2014).
70. Rao, C. N. R., Natarajan, S. & Vaidhyanathan, R. Metal Carboxylates with Open Architectures. *Angew. Chem. Int. Ed.* **43**, 1466–1496 (2004).
71. Galakhov, V. R. *et al.* Valence-band spectra and electronic structure of CuFeO₂. *Phys. Rev. B* **56**, 4584 (1997).
72. Joshi, T. *et al.* Structural and magnetic properties of epitaxial delafossite CuFeO₂ thin films grown by pulsed laser deposition. *J. Appl. Phys.* **117**, 013908 (2015).
73. Joshi, T., Senty, T. R., Borisov, P., Bristow, A. D. & Lederman, D. Preparation, characterization, and electrical properties of epitaxial NbO₂ thin film lateral devices. *J. Phys. Appl. Phys.* **48**, 335308 (2015).
74. Grundmann, M. *The physics of semiconductors an introduction including devices and nanophysics*. (Springer, 2006). at <<http://site.ebrary.com/id/10228998>>
75. Christy, A. A., Ozaki, Y. & Gregoriou, V. G. *Comprehensive Analytical Chemistry: Modern Fourier Transform Infrared Spectroscopy*. **XXXV**, (Elsevier, 2001).
76. Atkins, P. & de Paula, J. *Atkins' Physical Chemistry*. (Oxford University Press, 2006).
77. Benko, F. A. & Koffyberg, F. P. Opto-electronic properties of p- and n-type delafossite, CuFeO₂. *J. Phys. Chem. Solids* **48**, 431–434 (1987).
78. Harris, J. Simplified method for calculating the energy of weakly interacting fragments. *Phys. Rev. B* **31**, 1770 (1985).
79. Foulkes, W. M. C. & Haydock, R. Tight-binding models and density-functional theory. *Phys. Rev. B* **39**, 12520 (1989).
80. Demkov, A. A., Ortega, J., Sankey, O. F. & Grumbach, M. P. Electronic structure approach for complex silicas. *Phys. Rev. B* **52**, 1618 (1995).
81. Kurmaev, E. Z. *et al.* Electronic structure of niobium oxides. *J. Alloys Compd.* **347**, 213–218 (2002).
82. Agarwal, G. & Reddy, G. B. Study of surface morphology and optical properties of Nb₂O₅ thin films with annealing. *J. Mater. Sci. Mater. Electron.* **16**, 21–24 (2005).

83. Adler, D. Mechanisms for metal-nonmetal transitions in transition-metal oxides and sulfides. *Rev. Mod. Phys.* **40**, 714 (1968).
84. Weibin, Z. *et al.* The investigation of NbO₂ and Nb₂O₅ electronic structure by XPS, UPS and first principles methods: The investigation of NbO₂ and Nb₂O₅ electronic structure. *Surf. Interface Anal.* **45**, 1206–1210 (2013).
85. Posadas, A. B., O'Hara, A., Rangan, S., Bartynski, R. A. & Demkov, A. A. Band gap of epitaxial in-plane-dimerized single-phase NbO₂ films. *Appl. Phys. Lett.* **104**, 092901 (2014).
86. Wong, F. J., Hong, N. & Ramanathan, S. Orbital splitting and optical conductivity of the insulating state of NbO₂. *Phys. Rev. B* **90**, (2014).
87. Lee, J. C. & Durand, W. W. Electrically stimulated optical switching of NbO₂ thin films. *J. Appl. Phys.* **56**, 3350 (1984).
88. Pankove, J. I. Absorption edge of impure gallium arsenide. *Phys. Rev.* **140**, A2059 (1965).
89. Saito, K. & Ikushima, A. J. Absorption edge in silica glass. *Phys. Rev. B* **62**, 8584–8587 (2000).
90. Pankove, J. I. *Optical Processes in Semiconductors*. (Prentice-Hall, Inc., 1971).
91. Wang, Y. *et al.* Photoluminescence of colloidal YVO₄:Eu/SiO₂ core/shell nanocrystals. *Opt. Commun.* **282**, 1148–1153 (2009).
92. Riwotzki, K. & Haase, M. Wet-chemical synthesis of doped colloidal nanoparticles: YVO₄:Ln (Ln= Eu, Sm, Dy). *J. Phys. Chem. B* **102**, 10129–10135 (1998).
93. Seehra, M. S., Roy, P., Raman, A. & Manivannan, A. Structural investigations of synthetic ferrihydrite nanoparticles doped with Si. *Solid State Commun.* **130**, 597–601 (2004).
94. Nash, K. L., Rogers, R. D., Ferraro, J. & Zhang, J. Lanthanide complexes with 1-hydroxyethane-1, 1-diphosphonic acid: solvent organization and coordination geometry in crystalline and amorphous solids. *Inorganica Chim. Acta* **269**, 211–223 (1998).
95. Coates, J. in *Encyclopedia of Analytical Chemistry* 10815–10837 (2000).
96. Rall, J. D., Seehra, M. S. & Choi, E. S. Metamagnetism and nanosize effects in the magnetic properties of the quasi-two-dimensional system β -Ni(OH)₂. *Phys. Rev. B* **82**, 184403 (2010).
97. Tauc, J., Grigorovici, R. & Vancu, A. Optical Properties and Electronic Structure of Amorphous Germanium. *Phys. Status Solidi B* **15**, 627–637 (1966).
98. Tauc, J. Optical Properties and Electronic Structure of Amorphous Ge and Si. *Mater. Res. Bull.* **3**, 37–46 (1967).
99. Benko, F. A. & Koffyberg, F. P. The Optical Interband Transitions of Semiconductor CuGaO₂. *Phys. Status Solidi A* **94**, 231–234 (1986).
100. Manner, V. W., Kuposov, A. Y., Szymanski, P., Klimov, V. I. & Sykora, M. Role of Solvent–Oxygen Ion Pairs in Photooxidation of CdSe Nanocrystal Quantum Dots. *ACS Nano* **6**, 2371–2377 (2012).
101. Katari, J. B., Colvin, V. L. & Alivisatos, A. P. X-ray photoelectron spectroscopy of CdSe nanocrystals with applications to studies of the nanocrystal surface. *J. Phys. Chem.* **98**, 4109–4117 (1994).
102. Hines, D. A., Becker, M. A. & Kamat, P. V. Photoinduced Surface Oxidation and Its Effect on the Exciton Dynamics of CdSe Quantum Dots. *J. Phys. Chem. C* **116**, 13452–13457 (2012).
103. Powell, R. C. & Blasse, G. in *Structure and bonding* **42**, (Springer-Verlag).

104. Peng, X., Schlamp, M. C., Kadavanich, A. V. & Alivisatos, A. P. Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility. *J. Am. Chem. Soc.* **119**, 7019–7029 (1997).
105. Mohamed, R. M., Harraz, F. A. & Mkhaliid, I. A. Hydrothermal synthesis of size-controllable Yttrium Orthovanadate (YVO₄) nanoparticles and its application in photocatalytic degradation of direct blue dye. *J. Alloys Compd.* **532**, 55–60 (2012).
106. Jang, K. H. *et al.* Time-resolved luminescence spectroscopy of a YVO₄:Eu³⁺ thin film. *J. Lumin.* **129**, 1853–1856 (2009).
107. Hsu, C. & Powell, R. C. Energy Transfer in Europium Doped Yttrium Vanadate Crystals. *J. Lumin.* **10**, 273–293 (1975).
108. Singh, N. S., Ningthoujam, R. S., Luwang, M. N., Singh, S. D. & Vatsa, R. K. Luminescence, lifetime and quantum yield studies of YVO₄:Ln³⁺ (Ln³⁺ = Dy³⁺, Eu³⁺) nanoparticles: Concentration and annealing effects. *Chem. Phys. Lett.* **480**, 237–242 (2009).
109. Georgescu, S., Cotoi, E., Voiculescu, A. M. & Toma, O. Effects of particle size on the luminescence of YVO₄: Eu nanocrystals. *Romanian Rep. Phys.* **60**, 947–955 (2008).
110. Georgescu, S. *et al.* Optical and EPR investigations of the thermal treatment effects on YVO₄ nanocrystals. *Optoelectron. Adv. Mater. - Rapid Commun.* **3**, 1383 (2009).
111. Garces, N. Y., Stevens, K. T., Foundos, G. K. & Halliburton, L. E. Electron paramagnetic resonance and optical absorption study of V⁴⁺ centres in YVO₄ crystals. *J. Phys. Condens. Matter* **16**, 7095 (2004).
112. Millers, D., Yochum, H. M., Pankratov, V., Potera, P. & Grigorjeva, L. Transient and near-edge absorption in YVO₄ crystals. *Phys. Status Solidi C* **4**, 1155–1158 (2007).
113. Judd, B. R. Optical absorption intensities of rare-earth ions. *Phys. Rev.* **127**, 750 (1962).
114. Ofelt, G. S. Intensities of crystal spectra of rare-earth ions. *J. Chem. Phys.* **37**, 511 (1962).
115. Kirby, A. F., Foster, D. & Richardson, F. S. Comparison of 7FJ←5DO emission spectra for Eu(III) in crystalline environments of octahedral, near-octahedral, and trigonal symmetry. *Chem. Phys. Lett.* **95**, 507–512 (1983).
116. Kirby, A. F. & Richardson, F. S. Detailed analysis of the optical absorption and emission spectra of europium(3+) in the trigonal (C₃) Eu(DBM)₃.H₂O system. *J. Phys. Chem.* **87**, 2544–2556 (1983).
117. Zhang, J. *et al.* Photoluminescence studies of Y₂O₃:Eu³⁺ under high pressure. *J. Appl. Phys.* **115**, 023502 (2014).
118. Schmechel, R. *et al.* Luminescence properties of nanocrystalline YO: Eu in different host materials. *J. Appl. Phys.* **89**, 1679 (2001).
119. Moon, T. *et al.* Hydroxyl-quenching effects on the photoluminescence properties of SnO₂: Eu³⁺ nanoparticles. *J. Phys. Chem. C* **111**, 4164–4167 (2007).
120. Haas, Y. & Stein, G. Pathways of radiative and radiationless transitions in europium (III) solutions. The role of high energy vibrations. *J. Phys. Chem.* **75**, 3677–3681 (1971).
121. Klingshirn, C. F. *Semiconductor Optics*. (Springer, 2012).
122. Li, J. *et al.* Solar Hydrogen Generation by a CdS-Au-TiO₂ Sandwich Nanorod Array Enhanced with Au Nanoparticle as Electron Relay and Plasmonic Photosensitizer. *J. Am. Chem. Soc.* **136**, 8438–8449 (2014).
123. Berera, R., van Grondelle, R. & Kennis, J. T. M. Ultrafast transient absorption spectroscopy: principles and application to photosynthetic systems. *Photosynth. Res.* **101**, 105–118 (2009).

124. Rowley, J. D. *et al.* Broadband terahertz pulse emission from ZnGeP 2. *Opt. Lett.* **37**, 788–790 (2012).
125. Beard, M. C., Turner, G. M. & Schmittenmaer, C. A. Transient photoconductivity in GaAs as measured by time-resolved terahertz spectroscopy. *Phys. Rev. B* **62**, 15764 (2000).
126. Nienhuys, H.-K. & Sundström, V. Intrinsic complications in the analysis of optical-pump, terahertz probe experiments. *Phys. Rev. B* **71**, (2005).
127. Efros, A. L. Luminescence polarization of CdSe microcrystals. *Phys. Rev. B* **46**, 7448 (1992).
128. Pernik, D. R., Tvrđy, K., Radich, J. G. & Kamat, P. V. Tracking the Adsorption and Electron Injection Rates of CdSe Quantum Dots on TiO₂: Linked versus Direct Attachment. *J. Phys. Chem. C* **115**, 13511–13519 (2011).
129. Robel, I., Subramanian, V., Kuno, M. & Kamat, P. V. Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO₂ Films. *J. Am. Chem. Soc.* **128**, 2385–2393 (2006).
130. Tvrđy, K., Frantsuzov, P. A. & Kamat, P. V. Photoinduced electron transfer from semiconductor quantum dots to metal oxide nanoparticles. *Proc. Natl. Acad. Sci.* **108**, 29–34 (2011).
131. Ghanassi, M. *et al.* Time-resolved measurements of carrier recombination in experimental semiconductor-doped glasses: Confirmation of the role of Auger recombination. *Appl. Phys. Lett.* **62**, 78 (1993).
132. Klimov, V. I. & McBranch, D. W. Auger-process-induced charge separation in semiconductor nanocrystals. *Phys. Rev. B* **55**, 13173 (1997).
133. Sillen, A. & Engelborghs, Y. The correct use of ‘average’ fluorescence parameters. *Photochem. Photobiol.* **67**, 475–486 (1998).
134. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*. (Springer, 2006).
135. Dibbell, R. S. & Watson, D. F. Distance-Dependent Electron Transfer in Tethered Assemblies of CdS Quantum Dots and TiO₂ Nanoparticles. *J. Phys. Chem. C* **113**, 3139–3149 (2009).
136. Guijarro, N., Lana-Villarreal, T., Mora-Seró, I., Bisquert, J. & Gómez, R. CdSe Quantum Dot-Sensitized TiO₂ Electrodes: Effect of Quantum Dot Coverage and Mode of Attachment. *J. Phys. Chem. C* **113**, 4208–4214 (2009).
137. Robel, I., Kuno, M. & Kamat, P. V. Size-Dependent Electron Injection from Excited CdSe Quantum Dots into TiO₂ Nanoparticles. *J. Am. Chem. Soc.* **129**, 4136–4137 (2007).
138. Zhu, H. *et al.* Auger-Assisted Electron Transfer from Photoexcited Semiconductor Quantum Dots. *Nano Lett.* **14**, 1263–1269 (2014).
139. Cohn, A. W., Schimpf, A. M., Gunthardt, C. E. & Gamelin, D. R. Size-Dependent Trap-Assisted Auger Recombination in Semiconductor Nanocrystals. *Nano Lett.* **13**, 1810–1815 (2013).
140. Zhu, H., Song, N. & Lian, T. Controlling Charge Separation and Recombination Rates in CdSe/ZnS Type I Core–Shell Quantum Dots by Shell Thicknesses. *J. Am. Chem. Soc.* **132**, 15038–15045 (2010).
141. Roberti, T. W., Cherepy, N. J. & Zhang, J. Z. Nature of the power-dependent ultrafast relaxation process of photoexcited charge carriers in II–VI semiconductor quantum dots: Effects of particle size, surface, and electronic structure. *J. Chem. Phys.* **108**, 2143–2151 (1998).

142. Tisdale, W. A. *et al.* Hot-Electron Transfer from Semiconductor Nanocrystals. *Science* **328**, 1543–1547 (2010).
143. Hyun, B.-R. *et al.* Electron Injection from Colloidal PbS Quantum Dots into Titanium Dioxide Nanoparticles. *ACS Nano* **2**, 2206–2212 (2008).
144. Jin, S. & Lian, T. Electron Transfer Dynamics from Single CdSe/ZnS Quantum Dots to TiO₂ Nanoparticles. *Nano Lett.* **9**, 2448–2454 (2009).
145. Blackburn, J. L., Selmarten, D. C. & Nozik, A. J. Electron Transfer Dynamics in Quantum Dot/Titanium Dioxide Composites Formed by in Situ Chemical Bath Deposition. *J. Phys. Chem. B* **107**, 14154–14157 (2003).
146. J. S. Blakemore. *Semiconductor Statistics*. **3**, (Pergamon Press Inc., 1962).
147. Landsberg, P. T. Trap-Auger recombination in silicon of low carrier densities. *Appl. Phys. Lett.* **50**, 745 (1987).
148. Linnros, J. Carrier lifetime measurements using free carrier absorption transients. I. Principle and injection dependence. *J. Appl. Phys.* **84**, 275 (1998).
149. Cohn, A. W., Janßen, N., Mayer, J. M. & Gamelin, D. R. Photocharging ZnO Nanocrystals: Picosecond Hole Capture, Electron Accumulation, and Auger Recombination. *J. Phys. Chem. C* **116**, 20633–20642 (2012).
150. Linnros, J. Carrier lifetime measurements using free carrier absorption transients. II. Lifetime mapping and effects of surface recombination. *J. Appl. Phys.* **84**, 284 (1998).
151. Grivickas, V. & Jan Linnros. in *Characterization of Materials* 658 (John Wiley & Sons, Inc., 2012).