Ultrafast Charge Carrier Dynamics in Bare and Surface-Modified Semiconductor Nanoparticles

Jameel Abdul-Hadi Hasan
Western Michigan University, iameelahhasan@gmail.com

Follow this and additional works at: http://scholarworks.wmich.edu/dissertations
Part of the Chemistry Commons

Recommended Citation
http://scholarworks.wmich.edu/dissertations/741

This Dissertation-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Dissertations by an authorized administrator of ScholarWorks at WMU. For more information, please contact maira.bundza@wmich.edu.
ULTRAFAST CHARGE CARRIER DYNAMICS IN BARE AND SURFACE-MODIFIED SEMICONDUCTOR NANOPARTICLES

by

Jameel Abdul-Hadi Hasan

A dissertation submitted to the Graduate College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry Western Michigan University August 2015

Doctoral Committee:

 Ramakrishna Guda, Ph.D., Chair
 Sherine Obare, Ph.D.
 Ekkehard Sinn, Ph.D.
 Massood Atashbar, Ph.D.
ULTRAFAST CHARGE CARRIER DYNAMICS IN BARE AND SURFACE-MODIFIED SEMICONDUCTOR NANOPARTICLES

Jameel Abdul-Hadi Hasan, Ph.D.
Western Michigan University, 2015

Charge-carrier relaxation dynamics in semiconductor nanoparticles has been in the forefront of research for last three decades both for their fundamental nature as well as for applications in light-harvesting, luminescent labels, light-emitting diodes and nonlinear optics. Significant research has focused on II-VI semiconductors with emphasis on CdS and CdSe that are toxic. On the other hand, ZnO and TiO$_2$ semiconductor nanoparticles are less toxic and have enormous applications in photo-catalysis, water splitting, solar cells and optical sensors. However, the investigations of charge-carrier dynamics in these semiconductor nanomaterials compared to II-VI semiconductor quantum dots are quite limited. The knowledge of charge-carrier relaxation is essential to realize their optical applications. In this dissertation, efforts were made to probe ultrafast charge-carrier dynamics in bare ZnO and surface-modified TiO$_2$ nanoparticles with combined femtosecond fluorescence upconversion and transient absorption measurements.

Quantum-sized ZnO semiconductor nanoparticles show two luminescence bands corresponding to band-edge and trap-state luminescence where the dynamics of band-edge luminescence was not well understood.
In this dissertation, studies were carried out to probe the ultrafast band-edge luminescence dynamics in bare ZnO nanoparticles as a function of size. The measurements have shown interesting role of rate of trapping in the band-edge luminescence dynamics and conclusively shown that trapping dynamics dominates the charge-carrier relaxation. Along similar lines, ultrafast interfacial charge-transfer emission was monitored in small molecule-modified TiO$_2$ nanoparticles and have shown that small molecules create inter band-gap charge-transfer excitons that delocalize relatively fast into the conduction band of TiO$_2$ leading to efficient charge separation. In this study, results revealed that increasing the strength of donor leads to better charge separation. Ultrafast measurements on chromophore-surface modified TiO$_2$ nanoparticles have shown the role of localized charge-transfer excitons in charge separation and their use in dye solar cells. The results have shed light on heterogeneous interfacial charge-carrier relaxation dynamics in dye functionalized semiconductor nanoparticles. Finally, interesting trap-state luminescence of ZnO nanoparticles was used to develop turn-on luminescent dissolved oxygen (DO) sensors. Further, the sensitivity of ZnO nanoparticles towards DO was improved by preparing ZnO/graphene oxide nanocomposites that have shown additional ratiometric sensing capabilities for DO.
ACKNOWLEDGEMENTS

I would begin by acknowledging my very outstanding professor, mentor, and advisor Dr. Ramakrishna Guda. He has introduced me to very interesting avenues of science and provided the knowledge and work ethic needed to produce new ideas. He has always and will continue to stress the importance of understanding the fundamentals for education and research. I really enjoy learning various analytical techniques as I desired to.

I would like to thank every member of my graduate committee: From day one, Dr. Sherine Obare, for her continuing support throughout my progress toward obtaining this degree; Dr. Ekkehard Sinn thank for the jokes and your time; and Dr. Massood Atashbar thank you for you inspiration and especially for your time. I would like to acknowledge each and every laboratory group member and student past and present for Dr. Guda, who I have had the opportunity to produce research with. Thank you all for your steadfast support and making the time enjoyable and memorable.

I would like to acknowledge the Western Michigan University Department of Chemistry and the Western Michigan University Graduate College and more important for their support and provided programs for personal and professional development. Also the Michigan Alliances for Graduate and Education and the Professoriate (AGEP/MAGEP) for providing me with financial support and professional and development seminars and conferences throughout my time here at Western Michigan University.
I would also like to acknowledge all the students and registered student organization that I have been able to participate with and become members of which include the Muslim Student Association, the National Organization for the professional and educational advancement of Black Chemist and Chemical Engineers, COEXIST, and other organizations that I have been able to contribute to.

More importantly, I would like to acknowledge and thank my family for inspiring me and allowing me to move on and pursue my degree. I would like to especially acknowledge my mother and father for understanding and being patience with my decision thank you again.

Jameel Abdul-Hadi Hasan
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................ ii

LIST OF TABLES .................................................................................................................... x

LIST OF FIGURES .................................................................................................................. xi

1. INTRODUCTION AND BACKGROUND .......................................................... 1
   1.1. Basic Principles of Semiconductors ................................................................. 2
   1.1.1. Intrinsic and Extrinsic Semiconductors ..................................................... 3
   1.2. Direct and Indirect Semiconductors ............................................................... 4
   1.3. Density of States in Semiconductors ............................................................. 5
   1.4. Properties of Semiconductors at the Nanoscale ........................................... 6
   1.4.1. Surface to Volume Ratio ........................................................................... 7
   1.4.2. Quantum Size Effects ................................................................................ 7
   1.5. Effects of Size on Optical Properties ............................................................ 9
   1.6. Applications of Semiconductor Nanomaterials ............................................ 10
   1.6.1. Solar Energy Conversion and Dye Sensitized Solar Cells ...................... 10
   1.6.2. Photocatalysts .......................................................................................... 12
   1.6.3. Optical Sensors and Detectors ................................................................. 13
   1.7. Dynamics of Charge Carriers .................................................................... 15
   1.7.1. Charge Carrier Relaxation Pathways ..................................................... 16
   1.7.2. Effects of Surface Modification of Charge Carrier Dynamics .......... 17
Table of Contents—Continued

CHAPTER

1.7.3. Surface Modified TiO₂ Nanoparticles ........................................... 18
1.7.4. Monitoring the Charge Carrier Relaxation Pathways .......................... 19
1.8. Gap in the Field and Motivation ......................................................... 19
1.9. Research Approach ............................................................................. 20
1.10. Overall Dissertation Objectives .......................................................... 24
1.11. Scope of the Dissertation .................................................................... 25
1.12. Summary of Chapter 1 ....................................................................... 27
1.13. References ........................................................................................... 28

2. EXPERIMENTAL TECHNIQUES ............................................................. 33
2.1. Steady-state Methods .......................................................................... 33
  2.1.1. Optical Absorption Measurements ............................................... 33
  2.1.2. One Photon Fluorescence Measurements ...................................... 34
  2.1.3. Time-resolved Measurements ....................................................... 35
2.2. Fundamentals for a Laser ................................................................. 35
  2.2.1. Monochromatic Light Source ....................................................... 36
  2.2.2. Coherence ...................................................................................... 36
  2.2.3. Directionality ................................................................................ 37
  2.2.4. Short Pulse Capability ................................................................. 38
2.3. Nonlinear Optical Properties and Time-resolved Spectroscopy .......... 41
  2.3.1. Second and Third Harmonic Generation ...................................... 43
<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4. Ultra Laser Spectroscopic Techniques</td>
<td>46</td>
</tr>
<tr>
<td>2.4.1. Femtosecond Fluorescence Spectroscopy</td>
<td>47</td>
</tr>
<tr>
<td>2.4.2. Ultrafast Transient Absorption Spectroscopy</td>
<td>49</td>
</tr>
<tr>
<td>2.5. Dissolved Oxygen Testing</td>
<td>53</td>
</tr>
<tr>
<td>2.6. References</td>
<td>56</td>
</tr>
<tr>
<td>3. ULTRAFAST BAND EDGE LUMINESCENCE DYNAMICS OF ZNO NANOPARTICLES: SIZE VS TRAP STATES</td>
<td>61</td>
</tr>
<tr>
<td>3.1. Introduction</td>
<td>61</td>
</tr>
<tr>
<td>3.2. Materials</td>
<td>65</td>
</tr>
<tr>
<td>3.2.1. ZnO synthesis in 2-Propanol</td>
<td>65</td>
</tr>
<tr>
<td>3.2.2. ZnO synthesis in Ethanol</td>
<td>66</td>
</tr>
<tr>
<td>3.2.3. ZnO synthesis in DMSO</td>
<td>66</td>
</tr>
<tr>
<td>3.3. Methods</td>
<td>66</td>
</tr>
<tr>
<td>3.4. Results and Discussion</td>
<td>67</td>
</tr>
<tr>
<td>3.4.1. Optical Absorption and Steady-state Luminescence Measurements</td>
<td>67</td>
</tr>
<tr>
<td>3.4.2. Time-resolved Band Edge Luminescence Measurements</td>
<td>70</td>
</tr>
<tr>
<td>3.5. Conclusion</td>
<td>78</td>
</tr>
<tr>
<td>3.6. Summary of Chapter 3</td>
<td>79</td>
</tr>
<tr>
<td>3.7. References</td>
<td>80</td>
</tr>
</tbody>
</table>
# Table of Contents—Continued

4. ULTRAFAST CHARGE CARRIER DYNAMICS IN CATECHOL AND SALICYLIC ACID DERIVATIVES MODIFIED TiO_2 NANOPARTICLES…… 83

4.1. Introduction........................................................................................................ 83

4.2. Experimental..................................................................................................... 86

4.2.1. Materials........................................................................................................ 86

4.2.2. Synthesis of TiO_2 Nanoparticle................................................................. 87

4.2.3. Methods.......................................................................................................... 87

4.3. Results and Discussion ..................................................................................... 89

4.3.1. Optical Absorption Measurements............................................................. 89

4.3.2. Association Constants of Molecule/TiO_2 Nanoparticles:
Benesi-Hildebrand Analysis.................................................................................. 90

4.3.3. Femtosecond Luminescence Measurements............................................. 93

4.3.4. Transient Absorption Measurements......................................................... 98

4.4. Mechanism of Charge-Carrier Relaxation Dynamics in Surface-Modified
TiO_2 Nanoparticles............................................................................................... 108

4.5. Conclusion......................................................................................................... 110

4.6. Summary of Chapter 4...................................................................................... 113

4.7. References......................................................................................................... 114

5. ULTRAFAST INTERFACIAL CHARGE-TRANSFER DYNAMICS IN
ANTHRACENE AND PYRRENE CATECHOL FUNCTIONALIZED
TiO_2 NANOPARTICLES....................................................................................... 118

5.1. Introduction....................................................................................................... 118

5.2. Materials............................................................................................................ 121
## Table of Contents—Continued

### CHAPTER

5.2.1. Synthesis of TiO$_2$ Nanoparticles ........................................ 121
5.2.2. Fabrication of TiO$_2$ films ............................................. 122
5.2.3. Synthesis of (E)-4-((anthracen-2-ylimino) methyl) benzene-1,2-diol (AnthCat) ................................................................. 122
5.2.4. Synthesis of (E)-4-((pyren-1-ylimino) methyl) benzene-1,2-diol (PyrCat) ................................................................. 123

5.3. Methods .................................................................................... 124
5.4. Results and Discussion .............................................................. 126
  5.4.1. Optical Absorption Measurements ........................................ 126
  5.4.2. Association Constants of Molecule/TiO$_2$ Nanoparticles: Benesi-Hildebrand Analysis ................................................................. 127
  5.4.3. Femtosecond Fluorescence Upconversion Measurements ......... 128
  5.4.4. Femtosecond Transient Absorption Measurements ............... 132

5.5. Mechanism of Charge Carrier Pathways in DyeCat/TiO$_2$ Systems ........ 141
5.6. Conclusion .................................................................................. 143
5.7. Summary of Chapter 5 ............................................................... 144
5.8. References .................................................................................. 145

6. ZNO/GRAPHENE OXIDE NANOCOMPOSITES AS DISSOLVED OXYGEN SENSORS ................................................................. 150
  6.1. Introduction .............................................................................. 150
  6.2. Experimental ........................................................................... 152
<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2.1.</td>
<td>Material and Methods</td>
<td>152</td>
</tr>
<tr>
<td>6.2.2.</td>
<td>Synthesis of ZnO/GO Nanocomposites</td>
<td>153</td>
</tr>
<tr>
<td>6.3.</td>
<td>Results and Discussion</td>
<td>154</td>
</tr>
<tr>
<td>6.3.1.</td>
<td>Sensing of DO by ZnO</td>
<td>154</td>
</tr>
<tr>
<td>6.3.2.</td>
<td>Effect of ZnO Nanoparticle Size on the Sensitivity to DO</td>
<td>155</td>
</tr>
<tr>
<td>6.3.3.</td>
<td>Influence of Synthetic Conditions of ZnO on the Sensitivity to DO</td>
<td>158</td>
</tr>
<tr>
<td>6.3.4.</td>
<td>ZnO/GO Nanocomposites as DO Sensors</td>
<td>159</td>
</tr>
<tr>
<td>6.3.5.</td>
<td>Ratiometric Sensing of DO</td>
<td>161</td>
</tr>
<tr>
<td>6.3.6.</td>
<td>Mechanism of DO Sensing</td>
<td>162</td>
</tr>
<tr>
<td>6.4.</td>
<td>Conclusion</td>
<td>164</td>
</tr>
<tr>
<td>6.5.</td>
<td>Summary of Chapter 6</td>
<td>166</td>
</tr>
<tr>
<td>6.6.</td>
<td>References</td>
<td>167</td>
</tr>
<tr>
<td>7.</td>
<td>OVERALL SUMMARY AND FUTURE PERSPECTIVE</td>
<td>169</td>
</tr>
<tr>
<td>7.1.</td>
<td>Overall Summary</td>
<td>169</td>
</tr>
<tr>
<td>7.2.</td>
<td>Future Outlook</td>
<td>174</td>
</tr>
</tbody>
</table>
LIST OF TABLES

3.1 Luminescence decay lifetimes for ZnO in isopropanol............................................. 72
3.2 Luminescence decay lifetimes of ZnO/EtOH................................................................. 73

4.1 Association constants determined from Benesi-Hildebrand Analysis.......................... 92
4.2 Fluorescence lifetimes of the investigated small-molecule/TiO$_2$ nanoparticles.......... 95
4.3 Fluorescence lifetimes at different wavelengths for NO$_2$-Cat/TiO$_2$ composites......... 97
4.4 Transient decay times of the investigated small molecule/TiO$_2$ nanocomposites......... 105

5.1 The association constants for different Anth-Cat and Pyr-Cat TiO$_2$ Nanoparticles...... 128
5.2 Summary of ESA lifetimes for AnthCat in various media............................................. 138
5.3 ESA lifetimes of PyrCat in various media................................................................. 141
LIST OF FIGURES

1.1 Materials can be classified as insulators, semiconductors and conductors with specific valence and conduction bands, valence bands and energy gaps are associated with them................................................................. 2

1.2 Intrinsic semiconductors display pure structures while extrinsic Semiconductors are doped and defined as n-type (donor doped) or p-type (acceptor doped). $E_C$ is energy of conduction band, $E_F$ is the Fermi energy level, $E_D$ is the energy donor and $E_A$ is the energy acceptor............................................................. 4

1.3 Schematic representation of band structures for direct and indirect band gap semiconductors................................................................. 5

1.4 A display of electronic density of states of semiconductors from right to left 3, 2, 1, and zero degrees of freedom for electron movement........................................ 6

1.5 Changes in electronic energy levels going from a molecule to bulk semiconductor................................................................. 9

1.6 Absorption (A) and emission (B) spectra of ZnO nanoparticles display evidence of a change in the spectral optical properties in correlation to the quantum confinement resulting in a red shift for larger ZnO nanoparticles............................................................. 9

1.7 Representation of basic mechanistic operation of dye sensitized solar cell............. 11

1.8 Schematic diagram of depicting different surface reactions that occur at the interface of semiconductor nanoparticles................................................................. 13

1.9 Schematic illustration of charge carrier relaxation in semiconductor nanoparticles and small molecule modified semiconductor nanoparticles. Surface defect states and surface reactions play an important role at smaller sizes............................ 17

1.10 Schematic illustration of a surfactant modified TiO$_2$................................. 18

1.11 Schematic representation of the nanoparticle system investigated with different density of states................................................................. 21
1.12 (A) Surface passivated semiconductor nanoparticles with surfactants or molecules that just cover the surface without interacting with the surface of the semiconductor and (B) Other surface modified semiconductor nanoparticles that interact with the surface of semiconductor with the formation of charge-transfer states and modify the surface optically…………………………………………………… 23

1.13 Surface functionalization of semiconductor nanoparticle with a chromophore via a non-innocent surface modifier such as catechol that forms CT complex with the surface of semiconductor nanoparticle………………………………………………………………………………………………… 24

2.1 Schematic directionality and coherence . (A) Emitted light having coherence after passing a wavelength filter (B) incoherent light with uneven waves of emission (C) all individual wave are in phase along each axis giving it coherent properties………………………………………………………………………………… 37

2.2 Schematic of directionality of the beam displaying minor divergence of corrupt visible electromagnetic waves. Directionality of the beam displaying minor divergence of compact light waves……………………………………………………………………………………… 38

2.3 Schematic of display mode lock phenomena. The mode locked signal of modes aligned in fixed position in a three phase longitudinal modes……………………………………… 39

2.4 Fluorescence upconversion setup with second and third harmonic generation display. Schematic of the fluorescence upconversion setup for third harmonic that was used to carry out measurements presented in the dissertation…………………………………………………………………………………………………… 45

2.5 Second harmonic generation set up schematic of the fluorescence upconversion set-up that was used to carry out measurements presented in the dissertation. F1, F2, F3, F4 and F5 are filters. NC2 and NC3 are BBO crystals. ND is the neutral density filter. BS3 is the dichroic mirror. L3, L4, L5, L6 and L7 are lenses. PMT represents photomultiplier tube………………………………………………… 49

2.6 Femtosecond transient absorption set up. Schematic diagram of transient absorption setup. Spitfire generates amplified laser pulse at 800 nm. OPA is optical parametric amplifier. WLG is white light generation. CCD is the charge couple device……………………………………………………………………………………………………… 50
List of Figures—Continued

2.7 Transient absorption charge carrier dynamic processes. Different processes present in the transient absorption spectra (A) Excited absorption (singlet-singlet), (B) Bleach and (C) stimulated emission 52

2.8 Fluorimeter experimental set up for DO luminescence. Dissolved oxygen set-up for purging testing the emission 54

2.9 Experimental set of dissolved oxygen percent measurements. Dissolved oxygen reading set-up with Pasport DO probe 55

3.1 Cartoon diagram depicting the main objective of the investigation that was to show the influence of the size and rate of trapping on band edge luminescence dynamics 65

3.2 (A) Optical absorption spectra of ZnO nanoparticles synthesized in isopropanol taken at different times. (B) Luminescence spectra of ZnO synthesized with isopropanol. Emission spectra recorded at regular intervals during the growth of ZnO nanoparticles in 2-propanol excited at 310 nm 68

3.3 Plot of onset of absorption from Brus calculation and quantum mechanical calculation as a function of diameter of ZnO. This plot was used to calculate the sizes of ZnO nanoparticles 69

3.4 Optical absorption and steady-state luminescence spectra of ZnO nanoparticles synthesized using different methods 70

3.5 (A) Band edge luminescence decay traces obtained after excitation at 266 nm. All the decay traces were fit with exponential decay functions. (B) Plot of average lifetime as a function of nanoparticle size 72

3.6 Band edge luminescence decay traces obtained for ZnO prepared in the ethanol after excitation at 266 nm. All the decay traces were fitted with exponential decay functions 73

3.7 Band edge luminescence decay traces for ZnO DMSO obtained after excitation at 266 nm. All the decay traces were fit with exponential decay functions 74

3.8 (A) The intensity values of 3.9 nm sized particles plotted by the corresponding lifetime values. Average lifetimes plotted against the diameter of the different nanoparticle systems 75
List of Figures—Continued

3.9 (A) Luminescence spectra of 3.9 nm ZnO synthesized in different methods. (B) Plot of average lifetime versus the trap state to band edge luminescence intensity ratio.................................................................................................................................................. 76

3.10 Schematic diagram depicting the charge carrier relaxation dynamics in ZnO nanoparticles........................................................................................................................................................................ 77

3.11 Schematic diagram depicting the idea of defect states present within different ZnO nanoparticle systems prepared with different synthetical procedures. (A) ZnO with no defect states (B) ZnO prepared in alcohols IpOH and EtOH possess less defect-states (C) more are present in ZnO prepared in DMSO........................................................................................................................................... 77

4.1 Schematic diagram of surface charge-transfer (CT) modified TiO$_2$ nanoparticles……. 83

4.2 Molecular structures of the investigated small molecule derivatives.............................. 86

4.3 Optical absorption spectra of (A) catechol derivatives functionalized TiO$_2$ and (B) Salicylic acid derivatives functionalized TiO$_2$. Also shown for comparison in the absorption spectrum of bare TiO$_2$ nanoparticles in solution. Note the shift in absorption onset confirming the surface modification.......................................................................................................................... 90

4.4 Benesi-Hildebrand analysis of TiO$_2$/molecule charge-transfer complexes for (a) MetCat and (b) NO$_2$ Cat. It can be observed that there is one order of magnitude difference in the association constants with different substitution on the catechol........................................................................................................................................ 92

4.5 Fluorescence kinetic decay traces monitored for Cat/TiO$_2$ (A) at different emission wavelengths and corresponding anisotropy decay traces (B). Also shown are fluorescence kinetic decay traces at different emission wavelengths for (C) Sal/TiO$_2$ and corresponding anisotropy decay traces (D)............................................................................................................................................ 94

4.6 Femtosecond luminescence decay traces for different catechol derivatives on the surface of TiO$_2$ nanoparticles. (A) Similar luminescence kinetic decay comparison for Sal derivatives (B). ........................................................................................................................................... 95

4.7 Wavelength dependent luminescence decay traces NO$_2$-Cat/TiO$_2$ nanoparticles after excitation at 400 nm. (A) The anisotropy traces which show that the anisotropy is independent of emission wavelength and the excitation is fairly localized (B)............................................................................................................................................ 97
List of Figures—Continued

4.8 (A) ESA spectra at different time delays for Cat/TiO₂ after excitation at 420 nm. Corresponding transient decay traces at (B) 550 nm and (C) 675 nm........................................................................................................................ 100

4.9 (A) ESA spectra at different time delays for Sal/TiO₂ after excitation at 420 nm. Corresponding transient decay traces at (B) 505 nm and (C) 690 nm......................... 101

4.10 (A) ESA spectra at different time delays for MetCat/TiO₂ after excitation at 420 nm. Corresponding transient decay traces at (B) 480 nm and (C) 650 nm................................................................. 102

4.11 (A) ESA spectra at different time delays for NO₂-Cat/TiO₂ after excitation at 420 nm. Corresponding transient decay traces at (B) 480 nm and (C) 650 nm................................................................. 103

4.12 Comparison of kinetic decay at their ESA maxima for (A) Cat-derivatives/TiO₂ and (B) Sal derivatives/TiO₂................................................................. 105

4.13 (A) ESA spectra of Cat/TiO₂ thin film at different time delays and (B) kinetic decay trace comparison for solution and thin film phases................................. 107

4.14 (A) ESA spectra of Sal/TiO₂ thin film at different time delays and (B) kinetic decay trace comparison for solution and thin film phases................................. 108

4.15 Schematic diagram showing the CT complexation behaviors of catechol and salicylate with TiO₂ nanoparticles in solution. Also shown in the next schematic are the charge injection and charge delocalization pathways from the excited molecule/TiO₂ CT state.................................................. 109

5.1 Schematic diagram of the dye-surface CT modified TiO₂ nanoparticles.............. 119

5.2 Molecular structures of the investigated chromophores........................................ 121

5.3 Mechanistic scheme depicting the synthesis of AnthCat..................................... 123

5.4 Mechanistic scheme depicting the synthesis of PyrCat..................................... 124
List of Figures—Continued

5.5 Normalized optical absorption of AnthCat (A) and PyrCat (B) in methanol and on the surface of TiO$_2$ nanoparticles in solution and on thin films. Normalized fluorescence spectra of AnthCat (C) and PyrCat (D) in solution and on the surface of TiO$_2$ nanoparticles. Both dyes display quenched fluorescence when adsorbed to the surface of the TiO$_2$ nanoparticles ................................................................. 127

5.6 Absorption spectra of the investigated molecule/TiO$_2$ systems with an increase in TiO$_2$ concentration for (A) AnthCat/TiO$_2$ and (B) PyrCat/TiO$_2$................................. 128

5.7 Fluorescence decay traces of (A) AnthCat in methanol at 500 nm and (B) PyrCat in methanol at 480 nm. Also, shown in the insets are corresponding anisotropy decay traces ................................................................. 129

5.8 Femtosecond luminescence decay traces AnthCat/TiO$_2$ at different wavelengths ........................................................................................................ 131

5.9 Femtosecond luminescence decay traces for PyrCat/TiO$_2$ nanoparticles in solution at different emission wavelengths ........................................................................ 132

5.10 (A) ESA of AnthCat in methanol at time delays from 50 fs to 1.2 ps and (B) from 1.5 ps to 700 ps. (C) Species associated spectra obtained from global fit analysis ........................................................................................................ 133

5.11 (A) Excited state absorption of PyrCat in solution with (200 fs to 800 ps) time delays (B) Charge recombination trace monitored at 640 nm of the PyrCat free dye solution ........................................................................................................ 134

5.12 (A) ESA at different time delays for AnthCat/TiO$_2$ in solution after excitation at 420 nm. (B) Species associated spectra obtained from global fit analysis ........................................................................................................ 135

5.13 (A) ESA at different time delays for AnthCat/TiO$_2$ thin film after excitation at 420 nm. (B) Species associated spectra obtained from global fit analysis ........................................................................................................ 136

5.14 Kinetic decay trace comparison for AnthCatA/MeOH, AnthCat/TiO$_2$ in solution and on thin film and their ESA maxima ........................................................................................................ 137
5.15 (A) Excited state absorption of PyrCat/TiO$_2$ in solution at different time delays from 100 fs to 1 ns and (B) Species associated spectrum obtained from global fit analysis…………………………………………………………………………… 139

5.16 (A) ESA of PyrCat/TiO$_2$ thin films from 100 fs to 900 ps and (B) species associated spectrum obtained from global fit analysis………………………………………………………………………………………………………………………… 140

5.17 Kinetic decay trace comparison for PyrCat/MeOH. PyrCat/TiO$_2$ in solution and on thin film………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………...
6.9 Schematic diagram showing the mechanism behind the sensitivity of ZnO/GOnanocomposites. ................................................................. 164
CHAPTER 1

INTRODUCTION AND BACKGROUND

The electronic and optical properties of semiconductor nanomaterials have received enormous research attention for the last three decades for their applications in several areas such as optical detectors, photo-voltaics, sensors, lasers, catalysis etc. The main objective of this dissertation is to understand the optical properties of different semiconductor nanomaterials with an emphasis on their charge carrier dynamics. Monitoring charge carrier dynamics in semiconductor nanomaterials would help build better optical devices out of them. Also, the dynamics of charge carriers would help design and develop materials that are better suited for solar cells, sensors, and catalysis.

Bulk semiconductors are characterized by their band gap, fermi energy levels and their conductivities. On the other hand, at the nanoscale, semiconductors possess additional trap states, flat band potentials and reactions that make them quite interesting for both fundamental sciences as well as for applications. Excitation of semiconductors create electron-hole pairs or excitons and the charge carrier relaxation is dominated by the decay of excitons.\(^1\)\(^\sim\)\(^9\) At the nanoscale dimensions, surface-to-volume ratio (S/V) and quantum size effects play a major role in defining their optical and electronic properties.\(^3\)\(^\sim\)\(^5\) The unique optical, electronic and catalytic properties of semiconductor nanomaterials make them useful for applications in interdisciplinary areas of sciences. Before describing the optical properties of semiconductor nanomaterials, an overview of the semiconductors is provided.
1.1. Basic Principles of Semiconductors

Semiconductors, metals, and insulators are the three major categories of materials. All these possess a conduction band and a valence band, separated by a band gap as shown in Figure 1.1. The band gap is defined as the energy difference between the top of the valence band and the bottom of the conduction band. The valence band (VB) is composed of the electronic states with valence electrons and is fully occupied, and the conduction band is comprised of all the lowest unoccupied electronic states. As with the metals, the valence band and the conduction band are overlapped with the VB half-way occupied at times. Large band gaps separate the conduction and valence band and make up an insulator. All semiconductors contain shorter band gaps than insulators. It may be noted that materials that contain a band gap of 3.5 eV or lower can be classified as semiconductors. However, the band gap requirement is not a hard and fast rule, but the conductivities and optical properties define semiconductor materials.\textsuperscript{4,5}

![Figure 1.1](image_url)

**Figure 1.1** Materials can be classified as insulators, semiconductors and conductors with specific valence and conduction band, valence bands and energy gaps are associated with them
1.1.1. Intrinsic and Extrinsic Semiconductors

Semiconductors have different properties which allow them to be classified as either intrinsic or extrinsic. The intrinsic semiconductors, in principle, are considered to be free of defects or doping, and they have no electronic states in the band gap, making them less conductive.\textsuperscript{1-5,7,9} In practice, impurities and defects are present within the semiconductors which can manipulate the electronic and optical properties of the materials, giving them extrinsic properties. A schematic in Figure 1.2 gives an example displaying the difference between the intrinsic and extrinsic doped systems. In intrinsic semiconductors, the Fermi-energy level (an energy where the probability of finding an electron and hole is 0.5 eV) lies in the middle of conduction and the valence band. Extrinsic semiconductors can either be p-type or n-type. P-type semiconductors are characterized by doping of atoms that are electron deficient which makes the Fermi energy level close to the valence band and hole rich. On the other hand, n-type semiconductors are formed by doping electron rich atoms into an intrinsic semiconductor that makes the Fermi energy level closer to the conduction band. N-type semiconductors are electron rich. The p-type and n-type semiconductors make up the bulk of the electronics industry and have transformed human life in many ways.
Intrinsic semiconductors display pure structures while extrinsic semiconductors are doped and defined as n-type (donor doped) or p-type (acceptor doped). $E_c$ is the energy of conduction band, $E_F$ is the Fermi energy level, $E_D$ is the energy donor and $E_A$ is the energy acceptor.

1.2. Direct and Indirect Semiconductors

Semiconductors can be classified as either direct or indirect based on the band structure and they influence the absorption and emission characteristics. This variation is due to the nature of electronic band structures as shown in Figure 1.3. The electronic transitions are electrical dipole allowed within direct band gap semiconductors. This makes the absorption and emission allowed. ZnO is a direct band gap semiconductor and it has greater luminescence quantum efficiency. On the other hand, indirect band gap semiconductors are characterized by displaced higher potential energy surfaces and can only be reached with the help of a phonon. These phonon-assisted electronic transitions make both the absorption and emission of radiation weak. TiO$_2$ is one famous example of an indirect band gap semiconductor.
1.3. Density of States in Semiconductors

The density of states located in the conduction and valence bands of semiconductors play a crucial role in their electronic and optical applications. They are defined as the number of states per unit energy as seen in Figure 1.4. The electronic, chemical and optical properties of the semiconductors are affected by the density of states. In semiconductor structures, the density of states change as a function of the size and dimensionality of the particles. In semiconductor nanoparticles, electrons in the conduction band are delocalized throughout the particle, in this case the density of states rely on their dimensions. For bulk semiconductors, free movement of electrons in 3 dimensions is possible, and the density of states is exponential in nature. For thin films, where the electrons are confined in one direction and have a two-dimensional free electron movement the distribution for the density of states turns to be step-wise (Figure 1.4). For nanowires, electrons are confined in two dimensions but are free to move in one dimension and
the density of states follows wavering distribution. For quantum dots, where the electrons are confined in three dimensions, the density of states will be discrete and follow a particle in a box model. Other important aspects of semiconductors include: excitons, charge carrier mobilities, exciton radius, and oscillator strength and exciton binding energy. These fundamental properties allow them to be applicable in different areas. Excitons in semiconductors are Wannier-type excitons, where the electron and hole are loosely coupled, giving rise to free charge carriers at low temperatures.4,5,8,9,10

Figure 1.4. A display of electronic density of states of semiconductors from right to left 3, 2, 1, and zero degrees of freedom for electron movement9

1.4. Properties of Semiconductors at Nanoscale

As described above, the density of states in semiconductors depends mainly on the size and dimensionality of structures. Similarly, there are several other properties of semiconductors that will become important when the sizes of the particles are decreased. Some of the important properties of nanosized semiconductors are discussed here.
1.4.1. Surface to Volume Ratio

One important parameter that is clearly affected with a decrease in size of the semiconductor is the surface to volume ratio. This parameter separates the bulk and nano-sized semiconductors. For a solid spherical particle with a 1 centimeter diameter dispersed into 10 nm spherical particles, the surface area increases by a factor of 1 million. The S/V will increase drastically as the size of the particle is increased and this has important consequences for applications in catalysis, photo-degradation and other surface related semiconductor properties. Also, at the surface of semiconductor nanomaterials, the atoms are most unsaturated or possess different bonding environments, giving rise to surface trap states. The density of surface trap states also increases with a decrease in the size of the nanoparticle and this can affect optical, electronic and catalytic properties of semiconductors, which will be discussed later.

1.4.2. Quantum Size Effects

The most important parameter that influences the optical, electronic and magnetic properties of semiconductors with a decrease in size is that of the quantum confinement effect. When the size of the nanoparticle reaches the Bohr exciton radius (it is the radius of $^1S$ exciton wave function), the electrons’ and holes’ wave function vanishes at the boundaries that mandate an increase in energy as the excitons get frustrated at this size. The quantum confinement effect can be qualitatively explained by following the effective mass approximation. For a spherical semiconductor nanoparticle with a radius $R$, the effective band gap, $E_{g,\text{eff}}(R)$, is given by:

$$E_{g,\text{eff}}(R) = E_g(\infty) + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon R}$$

Equation 1.1
where, $E_{g(\infty)}$ is the bulk band gap, $m_e$ and $m_h$ effective mass quantities of the electron and hole, and $\epsilon$ is the bulk optical dielectric constant via relative permittivity. Effective band gap of semiconductor as a function of size depends on the bulk band gap and an additive term is related to the effective band gap which is inversely proportional to $R^2$. This term increases as the size of the particle decreases. The last term is a term that is responsible for describing Coulombic interactions.\textsuperscript{3,4,10,13,14} Quantum size effects are important when the particle sizes become compatible to the Bohar radius or smaller than the Bohr exciton radius. The following equation represents the Bohr exciton radius ($a_B$):

$$a_B = \frac{\epsilon_0 \hbar^2}{\pi \mu e^2}$$

\textbf{Equation 1.2}

and $\epsilon_0$ and $\epsilon$ are the permittivity of vacuum and the permittivity of the semiconductor, $\mu$ reduce mass of the exciton pair is given by $\mu$ and $e$ is the electron charge. For example, ZnO has a Bohr exciton radius of 1.8 nm and quantum size effects are observed below 4 nm. Likewise, quantum confinement effects are significantly observed in CdSe, CdS and GaAs semiconductors. A pictorial depiction of change in electronic energy levels as a function of size is shown in Figure 1.5.
**Figure 1.5** Changes in electronic energy levels going from a molecule to bulk semiconductor

1.5. Effect of Size on Optical Properties

As stated above, due to quantum confinement, decreasing the size of semiconductor nanoparticles will increase the band gap. However, this will decrease the area for the charge carriers to occupy their space, thereby restricting the exciton mobility.\(^1\)\(^-\)\(^8\),\(^10\)\(^-\)\(^13\) An example of change in size of ZnO nanoparticles as a function of time can be seen in absorption and luminescence spectra. With a decrease in particle size, the absorption spectra blueshifts indicating an increase in band gap with a decrease in particle size. This phenomenon is manifested in Figure 1.6A and Figure 1.6B that depicted the absorption and emission characteristics of ZnO nanoparticles, respectively.

![Absorption and Emission Spectra](image)

**Figure 1.6** Absorption (A) and emission (B) spectra of ZnO nanoparticles display evidence of a change in the spectral optical properties in correlation to the quantum confinement resulting in a red shift for larger ZnO nanoparticles.
1.6. Applications of Semiconductor Nanomaterials

Interesting and exciting properties of semiconductor nanomaterials make them suitable for several applications. Some of the current applications of semiconductor nanomaterials include light emitting diodes, solar cells, photo-detectors, security devices, quantum computing, sensors, biological imaging, photo-catalysts and nonlinear optical materials. Some applications that are of interest to the optical properties of semiconductor nanomaterials are presented here.

1.6.1. Solar Energy Conversion and Dye Sensitized Solar Cells

One of the major problems that mankind is facing is clean energy. Solar energy is one source of energy that is renewable and clean and has the potential to serve the growing needs of all people without any problem. Mother Nature has devised a pathway to create energy using sunlight in the form of photosynthesis. Taking a cue from nature, several attempts were made to develop better solar energy harvesting systems and solar cells with decent success. Silicon semiconductor based solar cells are the current norm for solar cells. In addition, other semiconductors such as CdSe, GaAs, InGaAs are actively used for making solar cells. Thin film semiconductor based solar cells have also shown good promise. Chemistry’s way of making solar cells is in dye-sensitized solar cells (DSSC) that actively uses semiconductor nanomaterials. DSSC’s have shown promise as cheap and environmentally benign options for solar cells. The principle of dye solar cells is that a dye (adsorbate molecules) molecule absorbs sunlight and gets excited, from where it injects electrons into the conduction band of the TiO$_2$ nanoparticles. The cycle is completed by the electrolyte replenishing the oxidized dye molecule. A schematic representation of dye solar cells is provided in Figure 1.8. The TiO$_2$ semiconductor nanoparticles provide the high surface area and interesting optical properties making them suitable for better charge separation, which is an important criterion for obtaining better solar energy.
conversion. In 1991, Gratzel demonstrated solar cell efficiency of 10% with ruthenium polypyridyl complex sensitized TiO$_2$ nanoparticles. Currently, the research has progressed and an efficiency close to 13% was achieved by them. For better solar cell efficiency, ultrafast electron injection and slow charge recombination are necessary. Enormous research attention is focused on understanding the charge transfer dynamics across molecule semiconductor nanocomposites, with an aim to find strategies to improve DSSC efficiencies. Similarly, researchers are also working on surface modified semiconductor nanoparticles to improve the solar cell efficiencies. Understanding the charge carrier dynamics in these semiconductor nanomaterials can shed light into their use in solar cells.

**Figure 1.7** Representation of basic mechanistic operation of dye sensitized solar cell
1.6.2. Photocatalysts

Another important area where semiconductor nanomaterials have played a huge role is in photocatalysis. Heterogeneous photocatalysis has garnered enormous research interest since the late 1970’s and early 1980’s and examined the avenues to produce clean and alternative fuels by photogeneration.\textsuperscript{59–64} TiO\textsubscript{2} again is the material of interest for these applications as it is routinely used for waste degradation and cleaning. TiO\textsubscript{2} photocatalysis is a major research avenue and has been used for several practical applications such as eradication of viruses, bacteria, and other microorganisms, odor control, deactivation of melanoma cells, production of hydrogen gas and cleaning oil spills.\textsuperscript{59,62–64} A perfect photocatalyst should be stable, non-toxic, economically viable, and highly photo-active. However, for a photocatalyst, the ability to separate charge carriers is as important as other parameters, as these charge carriers would generate necessary free radicals to either photocatalyze chemical reactions or degrade pollutants. The charge carrier dynamics and especially the dynamic interaction and reactions at the surface determine the overall quantum efficiency for catalysis.\textsuperscript{62} Various pathways reacting with electron donors and acceptors adsorbed on the surface of the photocatalyst arises from the trapped electrons and holes.\textsuperscript{64} Semiconductor nanomaterials such as TiO\textsubscript{2} offer enormous surface area for photocatalysis, but also photo-activate materials quickly to generate OH radicals at the interface in order to be effective for photocatalysis. Figure 1.10 schematically shows the generation of various photo-active materials upon photo-excitation of semiconductor nanomaterials. Organic pollutants are chemically oxidized into by-products of CO\textsubscript{2} and H\textsubscript{2}O on the surface of TiO\textsubscript{2}. Several oxidation and reduction reactions can take place on the surface of semiconductors due to the photoactive species created by photo-excitation. Investigations of charge carrier dynamics and various surface reactions at the interface of semiconductors would help researchers better design and develop more catalytic materials.
1.6.3. Optical Sensors and Detectors

Semiconductor nanomaterials are usually applied in the field of optical sensors. Optical sensing of pollutants, toxic materials, metal cations, anions is often carried by the use of semiconductor nanomaterials either by their electronic properties or optical properties. Notably, researchers have used the luminescent behavior of semiconductor nanoparticles to develop specific optical sensors that can be used in different disciplines of science and engineering. Semiconductor nanoparticles or metal oxides (for example TiO₂, SnO₂, ZnO) have been used for detection of toxic pollutants and combustible gases due to their rapid response time as well as other factors. As a part of this study, the use of ZnO with the incorporation of graphene oxide nanocomposites is used to sense the level of dissolved oxygen gases in different organic solvent systems which
could be used later and developed into an optical device for the detection of dissolved oxygen in different environments.\textsuperscript{66}

Another key aspect of semiconductor nanoparticles is their use in optical detectors. The development of commercial semiconductors began over forty years ago with the need to produce sensitive detectors for high frequency radiation; one reason for their use is their range of detectable wavelengths, because of their energy band gaps, along with the optoelectronic properties.\textsuperscript{68-72} Now these properties are being studied on at nanoscale dimensions where miniaturizing optical detectors have become important. So the future outlooks for semiconductor nanomaterial applications are endless and are being commercially incorporated with the latest detector and sensor advancements.

The basics of optical detectors lie within classical analytical spectroscopy. For example, a sample is placed in a defined path of radiation and the reacting light beam is detected. But within an optical detector, a light is guided out of a spectrophotometer, interacts with a sample and then is reintroduced to the spectrophotometer.\textsuperscript{70,69} Common optical detectors are based either on optical absorption or luminescence.\textsuperscript{72} Luminescence based detectors are more sensitive than those of absorption. Some of the well known luminescence based detectors are dissolved oxygen sensors which are based on luminescence quenching.\textsuperscript{71,72} Along similar lines, luminescent properties of semiconducting nanoparticles are put to use for developing better luminescence based detectors. However, to understand the mechanism of detection in these materials, investigations on charge carrier dynamics is necessary.

For all the above discussed applications of semiconductor nanomaterials, knowledge of the charge carrier dynamics will go a long way in designing and developing better materials for them.
A brief introduction into the dynamics of charge carriers and various charge carrier relaxation pathways is provided below.

### 1.7. Dynamics of Charge Carriers

As discussed earlier, charge carrier relaxation of semiconductor nanomaterials is important for their applications. Charge carriers in semiconductor nanoparticles constitute an electron and a hole. Photoexcitation creates an electron and hole and the recombination and separation of electrons and holes describe charge carrier dynamics. Also, charge carrier dynamics is not only important for bare semiconductors such as TiO$_2$ and ZnO but also for molecule functionalized semiconductor nanoparticles similar to that of interfacial charge transfer dynamics, except that in these systems, the dynamics are governed by the separation of electrons and cation radicals or anion radicals of adsorbates. Things to consider for the charge carrier dynamics of ZnO and molecule TiO$_2$ systems are the band gaps and trap states, because they alter the photoemission and absorption properties. In the research conducted for the dissertation, experiments were carried out to monitor the charge carrier dynamics and understand their role in semiconductor ZnO nanoparticles and surface modified-TiO$_2$ nanoparticle systems for possible use in nonlinear optical materials, solar cells and sensors.

The dynamics of charge carriers in surface modified semiconductor nanomaterials is better explained by interfacial electron transfer which was originally developed by Marcus, Gerischer, and Levich and Dogonadze in the late 1950’s and early 1960’s. The dynamics of charge carriers in bare and surface modified semiconductor nanomaterials are influenced by surface defect states. The charge transfer dynamics across the modified and semiconductor nanoparticles are also affected by the surface characteristics.
1.7.1. Charge Carrier Relaxation Pathways

The relaxation of photoexcited charge carriers follow systematic pathways. In bare semiconductor materials, electron and hole recombination occurs either radiatively or non-radiatively and they dominate the charge carrier relaxation. However, the surface defect states play a dominant role in trapping the electrons and holes that would complicate the relaxation dynamics. Conversely, for surface modified semiconductors, there are two main cases of relaxation. First one is via the electron emission case wherein photoexcited electrons are transferred to the surface adsorbate. The second case is the electron injection case, in which electrons are transferred from the optically excited surface modifiers to the conduction band of semiconductor material. This is important in understanding the interfacial electron transfer processes in the cathechol-TiO$_2$ systems presented in this work. Charge carriers have different pathways to follow and abide by transitions that gear them. Figure 1.11 displays some of the charge carrier pathways in correlation to the surface interactions. Photoexcitation leads to charge carriers and they relax and recombine, some radioactively, to give rise to band gap or surface state emissions.$^{10, 14, 27}$
1.7.2. Effects of Surface Modification on Charge Carrier Dynamics

As stated above, the surface states of the semiconductor nanoparticles will influence their optical and electronic properties. The high density trap states can be attributed to the dangling bonds that may have energies within the band gap separation. The charge carrier wave functions can become more localized as the deeper surface trap states lay within the band gap. Surface passivation by organic and inorganic molecules diminish the surface defect states and affect the photoluminescence from semiconductor nanoparticles. Several research reports are available where the surface of semiconductor nanoparticles are modified to achieve greater luminescent quantum efficiencies. It has been reported that band edge emission can be enhanced while
diminishing trap state emission via the removal of surface trap states. \(^4, 10, 23, 27\) The surface modification by direct adsorption of high extinction coefficient dyes in the visible absorption range can alter the charge carriers for photo-chemical and photo-electric applications.\(^{22-36}\)

1.7.3. Surface Modified TiO\(_2\) Nanoparticles

TiO\(_2\) nanoparticles have been applied in several areas as they are non-toxic, low cost, thermal and have photostability. \(^{52, 53, 56-58}\) They can also be supported by a variety of substrates. For example: glass fibers, stainless steel, inorganic materials, sand, as well as activated carbon.\(^{55-57}\) One thing that is not well known for TiO\(_2\) nanoparticles is their luminescence. However, luminescence was observed in surface modified TiO\(_2\) nanoparticles. Dodecyl benzene sulfonate modified TiO\(_2\) nanoparticles have shown emission in the visible region. (Figure 1.8) These particles also have interesting charge-transfer dynamics when chromophores are attached to it.

![Figure 1.10 Schematic illustration of a surfactant modified TiO\(_2\)](image)

\(^{4, 10, 23, 27}\) The surface modification by direct adsorption of high extinction coefficient dyes in the visible absorption range can alter the charge carriers for photo-chemical and photo-electric applications.\(^{22-36}\)
In the research presented here, surface modified TiO$_2$ nanoparticles were synthesized and the charge carrier dynamics were studied. The surface of TiO$_2$ nanoparticles was modified by small molecules that form charge-transfer complex with surface Ti$^{3+}$/Ti$^{4+}$ atoms and they significantly influence the charge carrier relaxation dynamics. They can have potential applications in solar cells and nonlinear optical materials.

1.7.4. Monitoring Charge Carrier Relaxation

Many techniques have been used in the literature to characterize the optical properties of semiconductor nanoparticles including microscopy, X-ray, and optical spectroscopy techniques.\textsuperscript{4, 7, 10, 37} The best techniques to monitor the charge carrier dynamics are time-resolved optical spectroscopic techniques, either that of absorption or luminescence. Femtosecond to nanosecond time-resolved absorption and luminescence measurements are routinely used to characterize the dynamics of charge carriers in bare and surface modified semiconductor nanomaterials. Time-resolved luminescence can probe both exciton recombination as well as exciton trapping. Complementarily, time-resolved absorption measurements are often used to follow both exciton relaxation as well as other pathways of charge separation and charge recombination. In the dissertation presented here, femtosecond time-resolved fluorescence measurements are mostly used while femtosecond transient absorption measurements are used in two projects.

1.8. Gap in the Field and Motivation

Charge carrier dynamics investigations provide the means to better optimize these materials for optical applications described above. Although an enormous amount of research is focused on the excited state dynamics of chromophores, corresponding studies of charge carrier dynamics in semiconductor nanomaterials are still lacking. After the discovery of size quantization
in semiconductor nanomaterials, several investigations have focused on understanding the role size plays on the dynamics of charge carriers. Good progress has been made in this area both theoretically and experimentally. However, along with change in size, the surface defects do change and that complicates the charge carrier dynamics. It is important for one to carry out systematic studies to differentiate the role of size or surface defects on charge carrier dynamics. One objective of this dissertation is to discern the role of size or surface trapping on the charge carrier relaxation dynamics in quantum sized semiconductor nanoparticles.

As noted above, surface modification has been used in many cases for synthesizing and passivating the nanoparticles and also in some cases to amplify the optical properties of the nanoparticles. Although a decent amount of work has focused on the charge carrier relaxation in bare semiconductor nanoparticles, similar work on surface modified semiconductor nanoparticles is lagging well behind. Understanding the dynamics would help the researchers to choose better ligands that can modify the optical properties for the betterment of the materials of interest. This is one motivation to monitor the charge carrier dynamics in surface-modified semiconductor nanoparticles especially that of TiO$_2$ with potential applications in solar cells and photo-catalysis. The objectives for this work are: (i) to monitor the charge carrier dynamics in small molecule modified TiO$_2$ nanoparticles that can form charge-transfer complexes with the surface of semiconductor nanoparticles and (ii) to probe the role of the surface modification on the electron injection and charge recombination with photoactive chromophores.

1.9. Research Approach

Smaller sized nanoparticles often possess dangling bonds that can be characterized as surface defects. Surface modification can passivate the surface to diminish the defects. To
accomplish the research objective of distinguishing the role of defect sites and size on charge carrier dynamics, synthesis and measurements of band edge luminescence were carried out on varying sizes of bare ZnO nanoparticles, which were synthesized with different methods to introduce various surface defect states. A schematic representation of the nanoparticles that were investigated was presented in Figure 1.13.

![Figure 1.11](image)

**Figure 1.11** Schematic representation of the nanoparticle system investigated with different density of states

Along parallel lines, surface modification is also employed to create novel semiconductor nanostructures whose properties are markedly different from the original semiconductor nanoparticles. Surface charge-transfer states are created in these surface modified nanomaterials. Although they are characterized by steady-state measurements, how the charge carrier dynamics is altered with surface modification is not clear. It is necessary to understand the charge carrier dynamics in these surface modified nanoparticles to optimally use them in applications. To
accomplish this objective, efforts were made to specifically introduce surface modification onto the surface of semiconductor nanoparticles with the use of small molecules that modify the surface of semiconductor nanoparticles optically. The surface of semiconductor nanoparticles can be modified by two ways. First is the surface passivation with innocent passivating agents that do not interfere with the semiconductor either optically or electronically (Figure 1.14, left). Secondly, is the modification of the surface of semiconductors with non-innocent ligands that alter both optical and electronic properties of semiconductor nanoparticles (Figure 1.14, right). There was also research carried out on surface passivation with innocent ligands. But, in this dissertation, efforts were focused on the surface modified semiconductor nanoparticles with charge transfer interaction that has potential for solar cell and catalysis applications.
Figure 1.12 (A) Surface passivated semiconductor nanoparticles with surfactants or molecules that just cover the surface without interacting with the surface of the semiconductor and (B) Other surface modified semiconductor nanoparticles that interact with the surface of semiconductor with the formation of charge-transfer states and modify the surface optically.

To further understand how the charge carrier dynamics would influence the interfacial charge transfer from chromophores, another set of semiconductor nanoparticles were investigated wherein organic chromophores were anchored to surface active semiconductor nanoparticles. The linker groups, or anchor groups, can alter the surface of semiconductor nanoparticles and can influence the charge transfer dynamics. In conventional dye sensitized semiconductor nanoparticle systems, a chromophore was bound to the surface of semiconductor by weak anchoring groups.
that cannot alter the surface of the semiconductor nanoparticle. An enormous amount of research was focused on understanding the charge transfer dynamics in these systems. However, it would be interesting to see how a reactive anchoring group on the surface would alter the charge transfer dynamics. So, the research approach for this part of the dissertation is to monitor the charge carrier dynamics in systems with reactive anchoring groups that are able one to find applications in solar cells and two-photon absorption materials. (Figure 1.15)

![Diagram](image.png)

**Figure 1.13** Surface functionalization of semiconductor nanoparticle with a chromophore via a non-innocent surface modifier such as catechol that forms CT complex with the surface of semiconductor nanoparticle

### 1.10. Overall Dissertation Objectives

This dissertation is aimed at filling the voids that are present in ultrafast charge carrier relaxation dynamics of semiconductor nanoparticles. The following concerns are addressed here:

(i) Understanding the role of size or surface defects in the charge carrier dynamics of widely used ZnO semiconductor nanoparticles, (ii) Exploring the role of surface charge transfer states on the charge carrier relaxation with small molecule modified semiconductor nanoparticles (TiO$_2$), (iii)
Understanding the role of surface charge transfer states in mediating forward electron transfer back recombination in a strategy similar to DSSC and (iv) Using quantum sized ZnO and ZnO/graphene oxide (ZnO/GO) architectures as optical sensors of dissolved oxygen.

1.1 Scope of the Dissertation

Chapter 2 describes the experimental techniques used for monitoring the optical properties of bare and surface modified semiconductor nanoparticles. A brief introduction to lasers and laser spectroscopic techniques is provided with an emphasis on time-resolved luminescence and transient absorption techniques that were used to monitor the charge carrier dynamics.  

Chapter 3 was aimed at understanding the role of size versus defect states on the dynamics of band edge luminescence dynamics in ZnO nanoparticles. The synthesis of ZnO nanoparticles with three different methods is described and their size was characterized with optical techniques. The dynamics that were monitored with femtosecond time-resolved luminescence with third harmonic generation was presented. It was determined from the results that the size of the nanoparticle plays only a minor role on the ultrafast relaxation but surface trapping and defect states influence greatly the charge carrier dynamics.

In Chapter 4, investigations were focused on understanding the charge transfer and charge carrier dynamics in small molecule modified TiO$_2$ nanoparticles. The surface of TiO$_2$ nanoparticle was modified with different catecholate and salicylate derivatives with varying donor and acceptor strengths. The dynamics of charge carriers was monitored with femtosecond time-resolved luminescence and transient absorption. The results have shown that with increasing the donor strength of the functional groups on the small molecules, charge recombination dynamics can be slowed down. A clear distinction between the charge-transfer complexation of catechol and salicylate was observed where former forms a complex with defect Ti$^{3+}$ states while the later forms
a complex with Ti\(^{4+}\). Also, the small molecule-TiO\(_2\) charge recombination is slowed down significantly on the surface of the TiO\(_2\) thin films as a reduction in the defect states that trap charges.

In chapter 5, ultrafast charge transfer dynamics of newly synthesized dye molecules, anthracene and pyrene catechol bound to TiO\(_2\) nanoparticles and thin films is presented. The dye molecules were synthesized via a Schiff base condensation reaction and the dynamics was monitored with ultrafast transient absorption and luminescence. The dynamics measurements have shown ultrafast charge injection and also faster charge recombination in solution while slower charge recombination was observed in thin films. The results have shown evidence for surface-state mediated charge recombination which was slowed down in thin films.

Chapter 6 details the use of ZnO nanoparticles for turn-on luminescence detection of dissolved oxygen. Most oxygen sensors work is based on luminescence quenching. This research has shown that ZnO can detect oxygen by turn-on sensing mechanisms. The effect of size on the sensing was monitored and the results show little relationship between the size of the nanoparticle and the sensitivity to oxygen. Also, measurements were carried out to improve the detection efficiency by attaching ZnO nanoparticles to graphene oxide. The results show that ratiometric sensing was better with ZnO/GO than ZnO alone. The dynamics of charge-transfer in ZnO/GO was monitored with femtosecond luminescence and the results have shown efficient charge transfer from ZnO to GO that was able to enhance the sensing ability of ZnO.

Finally, summary and future outlook for the research is provided in Chapter 7.
1.12. Summary of Chapter 1

- Semiconductor nanoparticles have shown promise for various applications across different disciplines because of their interesting optical, electronic and magnetic properties.
- The research presented in the dissertation has mainly focused on optical properties of semiconductor nanomaterials with applications in solar cells, photocatalysis, nonlinear optics and sensors.
- The importance of charge carrier dynamics and its role with semiconductor nanoparticles for applications is presented.
- This chapter highlighted the role of surface states and surface modifiers on the optical properties of semiconductor nanomaterials and the need for new studies to unravel the effects of surface modification on charge carrier dynamics.
- The main goal of the dissertation is to understand the charge carrier dynamics in environmentally benign ZnO and TiO$_2$ semiconductor nanoparticles.
- The research approach involved monitoring the luminescence of bare ZnO nanoparticles, surface modified and surface functionalized TiO$_2$ nanoparticles and ZnO/GO architectures.
1.13. References


CHAPTER 2

EXPERIMENTAL TECHNIQUES

Several analytical chemistry techniques are used traditionally to understand the optical properties of semiconductor nanomaterials.\textsuperscript{1-18} These include optical absorption, steady-state fluorescence, time-resolved fluorescence, and time-resolved absorption techniques. Optical absorption and fluorescence measurement help understand the energy shifts as a function of particle size and can also probe the electronic transitions of semiconductors with adsorbates. Ultrafast Fluorescence measurements by means of laser spectroscopy are used to monitor complex charge carrier dynamics in semiconductor architectures. These techniques are used to probe absorption, and scattering or emission of light, which hold important information about the unique properties of nanocomposite systems.

2.1. Steady-state Methods

2.1.1. Optical Absorption Measurements

Optical absorption (electronic absorption spectroscopy, UV-Vis) spectroscopy can give information about the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) transitions in molecules as well as band edge absorption in semiconductor architectures. It is based on the structure and environment of the sample being analyzed.\textsuperscript{1-3} For the experiments described in the dissertation, all absorbance measurements were recorded on a Shimadzu UV 2101 PC absorption spectrometer. The absorbance (A) of an absorbance species is related to the concentration (C) and molar extinction coefficient (\(\varepsilon_\lambda\)) a wavelength (\(\lambda\)) by the following equation:

\[
A = \varepsilon_\lambda C \times \text{path length (cm)}
\]
\[
A = \log \left( \frac{I_0}{I} \right) = \varepsilon_A Cl
\]  \hspace{1cm} \text{Equation 2.1}

where, \(I_0\) and \(I\) are the intensities of the incident and transmitted light, and \(l\) is the path length of the light beam that is passing throughout the cuvette (quartz) and the sample. All the measurements were carried out in a cuvette of path length 0.4 cm.

2.1.2. One Photon Fluorescence Measurements

Fluorescence spectroscopy is a complimentary technique to absorption and is more sensitive and provides information about the fate of the molecule or semiconductor after photo-excitation.\(^1\)\(^-\)\(^3\) Fluorescence or emission from semiconductor nanomaterials provide important information about the dynamics of charge carriers, which is the main focus of this dissertation. Steady-state emission spectra were recorded on an Edinburgh F900 spectrofluorimeter comprising a Xenon lamp as the excitation source, excitation and emission monochromators (M300) to avoid interference from the excitation and scattered radiation, and a Hamamatsu R955P as the detector which enabled data acquisition through a photon counting scalar card (PCS900). Steady-state emission spectroscopy is used to record the band edge as well as trap state luminescence in semiconductor nanostructures. Molecules or materials absorb light energy, leading to the excitation of an electron from low energy state to high energy excited state and the states relax either radiatively or non-radiatively.\(^1\)\(^-\)\(^3\) The fluorescence of the compounds is quantified by the excitation and emission peaks; here the difference in the wavelength maxima of the two readings is the Stokes’ shift (\(\Delta \nu, \text{cm}^{-1}\)) given by the following expression:

\[
\Delta \nu = \left[ \frac{1}{\lambda_{\text{abs(max)}}} \right] - \left[ \frac{1}{\lambda_{\text{em(max)}}} \right]
\]  \hspace{1cm} \text{Equation 2.2}

where, \(\lambda_{\text{abs(max)}}\) and \(\lambda_{\text{em(max)}}\) represent the maximum absorbance and emission in \text{cm}^{-1}.
2.1.3. Time-resolved Measurements

The central objective of the dissertation is to monitor the charge carrier dynamics in semiconductor architectures, and time-resolved measurements play a crucial role to probe them. Time-resolved optical characterization with femtosecond time resolution needs high intensity laser light sources for the excitation. As the dissertation deals with lasers and harmonic generation for the excitation of materials, a brief introduction to lasers and harmonic generation is provided here.

2.2. Fundamentals for a Laser

Laser or L.A.S.E.R. began as an acronym for the words ‘Light Amplification by the Stimulated Emission of Radiation’. A laser is a highly constructed segment of spectral waves making a very intense light source with unique characteristics that allow for its use in studying many things for various applications. One important application is its use to study nonlinear optical (NLO) properties of materials.\textsuperscript{4-18} The uniqueness of NLO materials lies within the attainability of the non-linear polarization from a laser source. Second harmonic generation (SHG), is the generation of higher energy light from produced from a ruby laser source passing through a quartz crystal, and it is one of the first NLO phenomenon discovered.

There are several components needed to create a basic laser that include an optical resonator, which contains the gain medium (active medium), and the external pumping source to achieve population inversion. The optical resonance should be achieved by two mirrors, a high reflector mirror and output coupler, that produce optical resonance from the reverberation of light between the two mirrors, which are engineered as curves to accelerate the resonant optical modes.\textsuperscript{4-18, 23} The main component of the laser is the gain medium where the lasing action occurs; it contains a collection of atoms and molecules which absorb and emit light.\textsuperscript{4-18, 23} Stimulated emission is an important component of lasing action where the emission of radiation is stimulated.
by another photon leading to two photons of same wavelength, direction and polarization. To achieve the needed stimulated emission, population inversion is very important and is achieved by an external source of energy called the pumping mechanism to populate a specific energy level of the laser. The pumping source can be an electrical current or optical excitation or chemical. All the lasers used in the dissertation have optical pump sources. The most important properties of laser radiation are briefly described here.

2.2.1. Monochromatic Light Source

A light source achieves monochromaticity once it possesses one single wavelength with a narrow bandwidth. This property gives laser beam sources its special characteristics. However, no laser can be absolutely monochromatic due to the uncertainty of light but can produce pure wavelengths of narrow bandwidths. Monochromaticity is inversely proportional to the line width which depends on the nature of the source and the gain medium. There are several laser sources that produce an array of bandwidth ranges.

2.2.2. Coherence

One unique property of laser radiation is coherence, which happens due to the stimulated emission that causes the emitted photons to be in harmony with one another, or “in step,” shown in Figure 2.1A. This will allow them to possess a definite phase relationship to one another which can be in the form of temporal coherence and spatial coherence which are independent of one another. In temporal coherence the waves are in phase and do not change within distance and time whereas spatial coherence does change over time (Figure 2.1B.)
2.2.3. Directionality

Directionality is simply a consequence that occurs due to the phase. The active material is placed in a resonant cavity and only the emission wave, which propagates along the cavity, can be sustained. Essentially, it propagates in a single direction of ideal harmony.\textsuperscript{23,24} The harmonious laser beams produce a compact source of light as it is focused and directed. This can be attributed to the partial coherence. However, because of divergence being diffraction limited, it allows the

\textbf{Figure 2.1} (A) Emitted light having coherence after passing a wavelength filter (B) incoherent light with uneven waves of emission (C) all individual wave are in phase along each axis giving it coherent properties
laser collimation properties to be credible. The laser brightness is a very important property. The brightness of light is due to a given source of electromagnetic waves, defining it as a power emitted per unit surface area, per unit of solid angle. The brightness of the laser is related to the directionality.

![Diagram showing laser beam directionality](image)

**Figure 2.2** Directionality of the beam displaying minor divergence of compact light waves

### 2.2.4. Short Pulse Capability

One of the most useful properties of the laser radiation for time-resolved spectroscopy is the ultra-short capability of the laser pulses, which makes them ideal for interrogating phenomenon happening at fast time scales. Lasers can be categorized as either being continuous wave (CW) or pulsed. During the early 1960s, the fastest pulses reached 10 ms duration with powers of kilowatts. Soon after the Q switching technique was introduced, pulse duration for laser radiations reached nanoseconds (ns) in power of megawatts. After the advent of the mode locking technique, possibilities of picoseconds pulse duration with a peak power of Giga watts was produced. With a special technique of colliding-pulse mode locking, femtosecond pulses were then generated. These type of lasers have been used in various applications for studying fast phenomena. Fast laser pulse or short time duration is an imperative component of a laser, which
is made possible by other subcomponents of the laser such as the Q-switching, cavity dumping and mode locking. Ultra-short laser pulses are obtained with the mode-locking technique. Mode locking technique is a construct that produces pulses of nanosecond and femtoseconds duration which can be used for nonlinear optical phenomena studies. A mixture of longitudinal and transverse modes with sporadic modes by mode relationships are produced by laser waves, oscillating solitary to one another. However, the technique of mode locking (or phase locking) is used to maintain a fixed phase harmony among the waves. In all, locking refers to the constant phase difference between different modes as can be seen in the following Figure 2.3.

Figure 2.3 Schematic displaying locked signal of modes aligned in fixed position in a three phase longitudinal modes

If we consider 2n+1 equivalent modes with an amplitude $E_0$, energy of a beam can be expressed as:

$$E(t) = \sum_{q=-n}^{n} E_q e^{i[(\omega_0 + q\Delta\omega)t + \varphi_q]}$$

Equation 2.3
where, $E_q$ is the amplitude of the $q^{th}$ mode, $\omega_0$ is the frequency of the central mode, $\Delta \omega$ is the angular frequency spacing in between the modes, and $\varphi_q$ is the phase of the $q^{th}$ mode. Essentially, this equation includes the summation of all modes, but with equal amplitudes, $E_0$, and constant successive modes, $\varphi_q - \varphi_{q-1} = \text{constant}$, then present equation will reduce to

$$E(t) = E_0 e^{i\omega_0 t} \sum_{q=-n}^{n} E_q e^{iq\Delta \omega t}$$  \hspace{1cm} \text{Equation 2.4}

It can be rearranged as:

$$E(t) = A(t) e^{i\omega_0 t}$$  \hspace{1cm} \text{Equation 2.5}

where $A(t)$ is given by:

$$A(t) = E_0 \sum_{q=-n}^{n} e^{iq\Delta \omega t}$$  \hspace{1cm} \text{Equation 2.6}

$q$ has variation from $-n$ to $n$ and a geometrical progression lies within expression $e^{iq\Delta \omega t}$ allow us to express the term as:

$$I(t) = \propto [A(t)]^2 = \frac{\sin^2[(2n+1)\Delta \omega t/2]}{\sin^2(\Delta \omega t/2)}$$  \hspace{1cm} \text{Equation 2.7}

where the intensity is given as a function of time. Essentially the following equation corresponds to a periodic function where high signal peaks emerge equivalently with leaks of uneven peaks lying in between them shown in the corresponding figure 5.3. The period ($T$) is given by the function $2\pi / \Delta \omega$ and the pulse duration $\Delta t$ can be expressed as:

$$2\pi / (2n + 1) = 1 / \Delta \nu$$  \hspace{1cm} \text{Equation 2.8}

In which $\Delta \nu$ is full width of the generation band. With varying amplitudes, the integration of the equation with infinite limits is given as:

$$A(t) = \int E_q e^{iq\Delta \omega t} \, dq$$  \hspace{1cm} \text{Equation 2.9}

This equation is representative of an integral from a Fourier transform function denoting the amplitude of a multi-mode output set by the transform of an amplitude distribution of modes in
the frequency domain, all within the time domain. If the mode locking of a continuum of oscillation
modes with a Gaussian distribution of amplitudes will display Gaussian pulses represented by the
equation:

\[ I(t) = \propto [A(t)]^2 \approx \exp \left[ -\ln 2 \left( \frac{2t}{\Delta \tau_p} \right)^2 \right] \]

Equation 2.10

with the period (\(\tau\)) expressed as

\[ \Delta \tau_p = \frac{2 \ln 2}{\pi \Delta \nu} = \frac{0.411}{\Delta \nu} \]

Equation 2.11

\(\Delta \tau_p\) and \(\Delta \nu\) are relative and \(\Delta \nu\) is composed from the equation:

\[ \Delta \nu = \frac{\Delta \lambda c}{\lambda_0^2} \]

Equation 2.12

Here \(\lambda_0\) is the wavelength at maximum amplitude, \(\Delta \lambda\) is the full width at half maximum and \(c\) is
the speed of light in nanometer per second. Thus, the short pulse duration is achieved from the
superposition of several waves leading to constructive interference at one place which leads to
short pulse laser generation and a frequency distribution of \(\Delta \nu\) and short pulse duration would be
achieved. Self mode locking is often seen with Ti:Sapphire laser which is used for all the
investigations. This is obtained by the fact that there is an intensitydependent change in the
refractive index making the Ti:Sapphire crystal to act as a soft aperture creating mode locking to
generate 100 fs pulses. With the short pulses obtained from Ti:Sapphire laser, various time-
resolved measurements were carried out.

2.3. Nonlinear Optical Properties and Time-resolved Spectroscopy

Nonlinear optical phenomenon is one of the important phenomena that make use of unique
properties of laser radiation. In 1961, Fraken and his colleagues used laser radiation to produce its
harmonics. More importantly, nonlinear effects such as laser frequency conversion have been
established to use in advancing applications within laser technologies for generating different wavelengths from the same fundamental frequency. This is important for the studies carried out in this dissertation because we needed different excitation wavelengths especially in the UV region. The techniques that are used to make different frequencies include: frequency mixing, optical parametric amplification (OPA) and optical parametric oscillation (OPO),\textsuperscript{31, 32, 33, 43} and harmonic generation such as second and third harmonic generation that were used widely for the investigations carried out in this dissertation. So, a brief description of NLO properties is provided here.

The fundamental laws of optics are embodied within Maxwell’s equations of electromagnetism, which are applied to all known materials. The Maxwell equations relate the current density to the electric field by the conductivity and the electric displacement to the electric field through the permittivity. The electric displacement $D$ is related to the electric field $E$ according to the equation:

$$D = \varepsilon \cdot E$$  \hspace{1cm}  \text{Equation 2.13}

Where $\varepsilon$ is the permittivity tensor. Usually, one can factor $\varepsilon$ into $\varepsilon = \varepsilon_0 \varepsilon_r$ where the permittivity of free space $\varepsilon_0$, the relative permittivity $\varepsilon_r$.

$$D \equiv \varepsilon_0 E + P$$  \hspace{1cm}  \text{Equation 2.14}

where $P$ is the polarization that is given by the electric dipole moment per unit volume (plus terms involving gradients of densities of higher electric multiple moments which seldom need to be considered and here disregarded. If we combine the equations, $P$ can be reorganized as:

$$P = \varepsilon_0(\varepsilon_r-1) \cdot E \equiv \varepsilon_0 \chi \cdot E$$  \hspace{1cm}  \text{Equation 2.15}
we can define the electric susceptibility tensor $\chi_n$. Within all linear materials, the response and stimulus are always proportional. For an example, induced polarization is proportional to the field and the susceptibility is independent of the field (always the case in practice at sufficiently low fields.) In high fields the polarization no longer is proportional to the field, so then susceptibility will depend on the field. From this we can then have a nonlinear response, which can be given by:

$$\frac{P}{\varepsilon_0} = \chi^{(1)} \cdot E + \chi^{(2)} : EE + \chi^{(3)}$$

Equation 2.16

where P, induced by an electric field, is proportional to electric field $E$. $\chi^{(1)}$ is the susceptibility tensor, $\chi^{(2)}$ the quadratic susceptibility tensor and $\chi^{(3)}$ the cubic susceptibility tensor. However, in practice, terms beyond cubic are not normally required. The quadratic susceptibility $\chi^{(2)}$ gives rise to second harmonic generation (SHG) in non-centro symmetric materials, the cubic susceptibility $\chi^{(3)}$ give rise to third-harmonic generation (THG) and following higher orders of nonlinear susceptibilities. For harmonic generation, it is important for the angular momentum should be conserved.

2.3.1. Second and Third Harmonic Generation

Different frequencies of laser were obtained from harmonic generation. Second harmonic generation (SHG) creates double energy photons, for example: 400 nm from a fundamental 800 nm laser. The other one that is used extensively in this dissertation is third harmonic generation (THG) that creates thrice the fundamental energy photons. For example, THG creates photons of 266 nm from the fundamental 800 nm. We were able to achieve femtosecond pulses in the UV region with the implementation of THG. The setup for THG is shown in Figure 2.4. The schematic can be explained as follows: A BBO crystal with a thickness of 0.5 mm was used to produce 400
nm pulses via SHG from an incident radiation of 800 nm. Close to 100 J of 400 nm was generated at the BBO and it was separated by a dichroic mirror which separates the fundamental 800 nm laser light from the 400 nm beam. THG was achieved by mixing the SHG beam at 400 nm with the fundamental 800 nm beam. However, for the sum frequency generation to be successful, both 400 nm and 800 nm should have the same polarization. Note that with SHG, 400 nm and 800 nm have a perpendicular phase relationship with one another. It is important to change the polarization of one of the beam to achieve proper sum frequency generation for THG. This was achieved by first directing the second harmonic beam through a polarization rotation mirror setup and mixing the SHG beam and the fundamental beams at another BBO crystal to generate a sum frequency beam of 266 nm. For successful production of 266 nm, both beams should overlap both in space and time which is controlled by a delay line. The fundamental equations involved in SHG, THG and sum-frequency generation are described here.

Essentially, SHG is a nonlinear optical production of the second order or the doubling of frequencies from the laser radiation with the given formula:

\[ \omega_2 = \omega_1 + \omega_1 \]  \hspace{1cm} \text{Equation 2.17}

Here \( \omega_1 \) is the optical frequency of the laser radiation and \( \omega_2 \) is the optical frequency of the second harmonic. In order for this SHG to become efficient there should be focused-phase matching that can function in an anisotropic crystal with different polarizations from the operated laser radiation along with the second harmonic frequency. Simultaneously, there should be a phase matching angle that is between the laser beam propagation and the crystal optic axis. The phase matching can be represented by the following equation:

\[ k_2 = k_1 + k_1 \]  \hspace{1cm} \text{Equation 2.18}
where $k_1$ is the wave vector of the fundamental radiation and $k_2$ is the wave vector of the operated laser radiation.

THG is a second order nonlinear optical effect like SHG, but it involves the mixing of two beams to generate a high frequency beam. For THG, a beam from SHG and fundamental are mixed. The SFG can be described as:

$$\omega_3 = \omega_1 + \omega_2$$  \hspace{1cm} \text{Equation 2.19}

but, it needs proper mixing of the angular momentums as well described by:

$$k_3 = k_1 + k_2$$  \hspace{1cm} \text{Equation 2.120}

THG results from the sum frequency generation between the fundamental laser radiation and the second harmonic pulses at a relative phase matching angle of the nonlinear crystal.

\textbf{Figure 2.4} Fluorescence upconversion setup with second and third harmonic generation display. Schematic of the fluorescence up conversion set-up for third harmonic that was used to carry out measurements presented in the dissertation.
2.4. Ultrafast Laser Spectroscopic Techniques

The analytical practices of ultrafast lifetime spectroscopic techniques have become an interdisciplinary area of research which incorporates the mechanistic and kinetic analyses associated with charge carrier dynamics of different chemical systems to be recorded using femtosecond, picosecond, and nanosecond time scales. Its use in the sub-fields of inorganic chemistry and solid state physics allows for the probing of multi-exciton effects, measuring of interaction energies and the determination of material constants. The idea behind these techniques is to excite the nanocomposite systems with a short femtosecond (picosecond, nanosecond) light pulse and monitor the changes in excited states with a second (delayed) laser pulse. Two main time-resolved laser techniques that are used in the present study are time-resolved fluorescence and time-resolved absorption that can monitor the fluorescence and excited state absorption of materials, respectively.

2.4.1. Femtosecond Fluorescence Spectroscopy

Time-resolved fluorescence is monitored in most cases using time-correlated single photon counting whose time-resolution is limited by the electronics. It would be difficult to get better than 20 ps time resolution using this technique even with the best of electronics. However, charge carrier dynamics in semiconductor nanoparticles can be fast, so a technique that can follow these processes is necessary. One such time-resolved fluorescence technique is femtosecond fluorescence upconversion or a time-gated sum-frequency generation technique. The time resolution in fluorescence upconversion arises from the optical delay between the pump and probe, not on the electronic response of the detectors. So, the time-resolution is limited by the pulse width.
of the laser. In the fluorescence upconversion set up, a gate pulse and a fluorescence signal obtained from laser excitation are merged on a nonlinear crystal to generate SFG signal, which is termed as the upconversion signal. This upconverted signal is monitored as a function of optical delay between the gate pulse and the fluorescence signal, monitoring the fluorescence decay process or emission decay processes. \(^{23, 28, 31, 33, 36, 37}\) Mathematically, the upconversion signal \((\omega_{\text{sum}})\) from the BBO crystal can be given by the following equation:

\[
\omega_{\text{sum}} = \omega_{\text{laser}} + \omega_{\text{fl}}
\]

**Equation 2.20**

where \(\omega_{\text{laser}}\) and \(\omega_{\text{fl}}\) are gate frequency and fluorescence frequency, respectively. This equation can be rewritten in terms of wavelengths as:

\[
\frac{1}{\lambda_{\text{sum}}} = \frac{1}{\lambda_{\text{laser}}} + \frac{1}{\lambda_{\text{fl}}}
\]

**Equation 2.21**

the function \(\lambda_{\text{sum}}\) is the wavelength of the resulting sum-frequency signal, \(\lambda_{\text{laser}}\), is the fundamental wavelength from the laser, and \(\lambda_{\text{fl}}\) is the wavelength of the fluorescence signal. The radiated intensity of the up converted signal via sum-frequency signal is represented by the following equation:

\[
I_{\text{sum}}(\tau) = \int_{-\infty}^{\infty} I_{\text{fl}}(t) I_{\text{laser}}(t - \tau) \, dt
\]

**Equation 2.22**

in which \(\tau\) is the time delay between the fluorescence and the gating pulse and \(t\) us the lifetime. The fluorescence upconversion system used in presented experiments was obtained from a CDP system. A schematic of the setup used for presented measurements is shown in Figure 2.5. Our system used both SHG and THG frequencies from a mode locked broadband Ti-Sapphire laser (Spectra Physics, Tsunami, 800 nm). The sample is continuously rotated with a rotating cell which is 1 mm thick to avoid the degradation of the sample. The fluorescence emitted from the sample was up converted in a nonlinear crystal of BBO with the pump beam at 800 nm, which first passed
through a variable delay line. The instrument response was measured by the use of Raman scattering from water. A double monochromator with a photomultiplier tube was used to achieve the necessary resolution. Time-resolved fluorescence anisotropy measurements were carried out with parallel and perpendicular excitations whose polarization is changed with a Berek compensator. Fluorescence anisotropy \( r(t) \) is calculated from the traces obtained after parallel (\( I_{\text{par}} \)) and perpendicular (\( I_{\text{per}} \)) excitation with the following equation which is based on the ratio of the difference between parallel and perpendicular polarized emissions over magic angle fluorescence.

\[
    r(t) = \frac{I_{\text{par}}(t) - G I_{\text{per}}(t)}{I_{\text{par}}(t) + 2G I_{\text{per}}(t)}
\]

Equation 2.23

where the G factor accounts for the differences in sensitivities for the detection of emission in the perpendicular and parallel polarized configurations. The G factor was obtained from the tail fitting of the anisotropy decays of perylene in methanol and Coumarin 485 in methanol.
Figure 2.5 Second harmonic generation schematic of the fluorescence up conversion setup that was used to carry out measurements presented in the dissertation. F1, F2, F3, F4 and F5 are filters. NC2 and NC3 are BBO crystals. ND is the neutral density filter. BS3 is the dichroic mirror. L3, L4, L5, L6 and L7 are lenses. PMT represents photomultiplier tube.

2.4.2 Ultrafast Transient Absorption Spectroscopy

To investigate the ultrafast phenomena and charge carrier dynamics in semiconductor nanomaterials, transient absorption spectroscopy via pump-probe spectroscopy was used.\textsuperscript{44, 45, 46} Even in the pump-probe spectroscopy, time resolution is achieved via an optical delay between pump and the probe pulse. The pump beam excites the sample and probe beam monitors the excited state absorption, stimulated emission or bleach of the ground state. The change in absorbance ($\Delta A$) is monitored as a function of optical delay between the pump and probe beam as well as a function of wavelength. The given spectral readings may then be expressed in a three-dimensional view from which various data interpretations can be obtained. Figure 2.6 depicts the schematic of the transient absorption used for the described measurements presented in this dissertation.
Femtosecond transient absorption measurements were carried out at the Center for Nanoscale Materials, Argonne National Laboratory.\textsuperscript{33,37} To briefly explain, a Spectra Physics Tsunami Ti:sapphire @75 MHz oscillator was used to seed a 1.66 KHz Spectraphysics Spit-Fire Pro regenerative amplifier with a 100 fs pulsewidth. Ninety-five (95\%) of the output from the amplifier is used to pump a TOPAS optical parametric amplifier, which is used to provide the pump beam in the Helios transient absorption setup (Ultrafast Systems Inc.) The remaining five percent (5\%) of the amplifier is focused onto a sapphire crystal to create a white light continuum that serves as the probe beam in our measurements (430 to 780 nm). The pump beam was depolarized and chopped at 833 Hz, and both pump and probe beams were overlapped in the
sample. The average power of the pump was kept at 200 nJ per pulse and the early time transient decay traces were found to be pump power independent. The samples were measured in a 2 mm quartz cuvette and also on thin films that were moved periodically with a stepper motor.

Transient absorption spectral data includes three main features as shown in Figure 2.7. One is a positive feature which is called excited state absorption (ESA). ESA is positive as we are monitoring the excited states of molecules or materials that are created by photo excitation. The pump beam excites the sample and creates population in the excited state. The probe beam, which is a broad band of wavelengths, can be absorbed by the excited state which reduces its intensity. As the change in absorption monitors the intensity of the probe beam before and after photo excitation, the signal should be positive. The ESA of molecules or materials can be due to several reasons: it can be either due to singlet-singlet absorption or triplet-triplet absorption of charge carriers absorption; or cation/anion radical absorption. With time, the excited states or charge carriers relax and the change in absorption reduces thus monitoring the charge carrier dynamics.

The secondary contribution to transient absorption signals is the stimulated emission which is a negative signal. Stimulated emission occurs from molecules or materials, in which, where the emission is stimulated by the incoming probe photon. When the pump is not there, we have distinct probe intensity, but with the pump on you have additional emission intensity that is stimulated by the probe beam. The intensity would be higher with the pump than without pump thus leading to negative change in absorption. The stimulated emission would occur at the emission wavelength of the material. The third contribution to transient absorption spectra, which leads to a negative signal is due to the bleach of the ground state. This is a negative signal because of the following reasons; when the pump is not present, the probe beam would be absorbed significantly
near the ground state absorption of the material. With the pump beam exciting the sample, a significant fraction of the ground state reaches the excited state. This is done when the probe beam monitoring the ground state absorption of the material records less of the material and there by less probe beam is absorbed. In this way, the probe intensity would be higher without the pump than with the pump beam. This leads to a negative change in absorbance. The way to differentiate the two negative absorptions, is by checking where the negative signal arises. If it arises at the absorption of the material, it is considered a bleach signal and if the negative signal’s wavelength matches that of emission spectrum, it can be attributed to stimulated emission of the material.

**Figure 2.7** Different processes present in the transient absorption spectra (A) Excited absorption (singlet-singlet), (B) Bleach and (C) stimulated emission
2.5. Dissolved Oxygen Testing

One of the important applications that were discussed in the dissertation is that of sensing dissolved oxygen (DO) in samples via novel approaches. To test our new system, it is important to describe the existing methodologies to test dissolved oxygen. There are a variety of methods that are used to sense DO. The most common method is the Winkler titration method. This is based on the oxidation of bivalent manganese (a manganese hydroxide) by the oxygen dissolved in the water that produces a tetravalent compound followed by acidifying and changing the color of the sample by oxidizing the potassium iodide releasing iodine. The amount of iodine is chemically equivalent to the amount of DO that is present in the sample. This method has several limitations such as opaqueness in the water due to turbidity and chlorophyll. It would be ideal if there were a method based on fluorescence rather than the absorbance of a material.

Another apparatus for DO detection is the polarographic method or electrochemical membrane sensor method commonly used for in situ experimental analysis, which are usually referred as Clark type measurements. Clark type electrodes operate on polarographic principle wherein the oxygen contained in the sample solution comes in contact with a gas permeable layer and enters the membrane and changes its potential by coming into contact with the electrode. When the oxygen reacts with the cathode, the created boundary allows the cathode concentration to be zero, producing a current that is based on the interaction of diffusion through the cell. The common factors that affect the capabilities are the membrane transport properties, the electrolyte properties, the cathodic properties, and boundary layer thinness at the membrane. However, method cannot be used as the membrane is sensitive to harsh environments. Other methods used are dynamic luminescence quenching methods which began in 1939. These methods work based
upon the principle of quenching of the phosphorescence from the triplet state of oxygen. Although this principle is based on luminescence quenching, it is not sensitive to low concentrations of the oxygen. This technique is still being used commercially but requires alternative methods that can improve its performance.\textsuperscript{51}

For the DO readings, we have used a Clark type electrode connected to PasPort XLS and calibrated it with Data Studio software. This electrochemical probe measures the electric current obtained from a chemical response due to the reduction of the oxygen molecules and the oxidation of the silver atom on the end of the cathode electrode. The setup of the experiment can be seen in the Figure 2.8. Figure 2.9 is a schematic experimental setup representation of the ZnO/GO sample being tested for DO content. Further explanation of the DO and luminescence properties of ZnO/GO will be explained in Chapter 6.

![Figure 2.8 Dissolved oxygen set-up for purging testing the emission](image-url)
Figure 2.9 Dissolved oxygen reading set-up with Pasport DO probe
2.5. References


18. Pedro, A. Quinto-Su, Venugopalan, V. Laser Microbeam and Medical Program Beckman Laser Institute, University of California, Irvine, California 92612.


21. [http://www.mrl.columbia.edu/ntm/level1/ch02/html/l1c02s02.html](http://www.mrl.columbia.edu/ntm/level1/ch02/html/l1c02s02.html)


27. [www.df.unipi.it/~fisapp/Gruppi/Metrologia/spiegazioni/boris.pdf](http://www.df.unipi.it/~fisapp/Gruppi/Metrologia/spiegazioni/boris.pdf)


3.1 Introduction

The central goal of the dissertation is to probe the charge carrier dynamics in semiconductor nanoparticles with an overall aim to design and develop better nanomaterials for optical applications. The first semiconductor materials to show quantum confinement were sulfides and oxides of Zn were observed by Brus and co-workers. Since the discovery of quantum size effects in semiconductor nanostructures, an enormous amount of research has focused on developing better quantum confined systems for biological imaging, sensors and solar cells. To accomplish the objective of monitoring the charge carrier dynamics in semiconductor quantum dots, one of the well investigated semiconductors that show quantum confinement (ZnO) was chosen.

Since the discovery of quantum confinement in semiconductor nanoparticles in the early 1980s, significant research was focused on using quantum sized semiconductor nanomaterials for several applications such as biological labels, light emitting diodes, sensors, catalysts etc. Among several semiconductors investigated, ZnO is especially interesting as it is non-toxic, thermally and chemically stable, and possess intense luminescence both in UV and visible region. It has found applications in interdisciplinary areas of sciences that include solar cells, sensors, light-emitting diodes, biological and terrestrial applications. Several ZnO morphologies have been reported in literature that included nanowire, nanorod, tetrapods, nano ribbons, nano belts, nano trees, and
nano forest intended for optical applications.\textsuperscript{17-22} The most recent developments of ZnO are toward synthesizing zero-dimensional ZnO clusters by condensation, thermal vapor transport, polyol methods, thermolysis, micro emulsion precipitation, and sol-gel methods. In addition to various geometric structures, optical properties of ZnO have been well investigated for their applications as chemical sensors, solar cell materials, optoelectronics and nonlinear optical materials.\textsuperscript{1-16, 23-38}

Among different characteristics of ZnO nanoparticles, optical properties are very interesting and have been subjected to significant research for last three decades. They show size dependent absorption that can be explained by Brus’s equation of quantum confinement. Also, they show two luminescence peaks, one near the onset of absorption (mostly in UV) and another broad emission in the visible region. The emission in the UV region is sharp and is assigned to band-edge luminescence which arises from the recombination of electrons and holes that relax close to the band edge. The visible luminescence is assigned to the emission from the surface states or trap states. An enormous amount research efforts were focused on understanding the origin of this visible luminescence by different groups. At present, the consensus is that this luminescence arises out of electrons trapped in shallow trap states recombining with the oxygen vacancies (or deep trapped holes). This mechanism for visible luminescence explains the fact that saturating the surface of ZnO with oxygen quenches this visible luminescence and removing oxygen from the solution regenerates this luminescence. Also, Kamat and co-workers have shown “sense and shoot approach” with the idea that the visible luminescence was quenched by adding catecholate molecules which can be degraded by shooting UV radiation which will destroy the molecules and the visible emission of nanoparticle is regenerated.\textsuperscript{39}

In addition to steady-state optical properties of ZnO quantum dots, several researchers have also studied their time-resolved optical properties. However, most of the research efforts were
focused on monitoring the trap state luminescence. The lifetime of visible luminescence was found to be long with lifetimes in the microsecond region. But, even here the lifetimes were found to be dependent on the synthetic methodology used and the architectures that were created. In addition to microsecond lifetimes, some research groups have also observed lifetimes in nanosecond time domain. In a recent work, Papanikolas and co-workers\textsuperscript{40} have monitored visible luminescence in ZnO nanorods and observed nanosecond lifetimes. Temperature-dependent visible luminescence dynamics ZnO in isopropanol from 10 to 60 Celsius have shown small changes in the lifetime that remained in microsecond region. Few studies have focused on the charge carrier dynamics in ZnO nanoclusters especially in the ultrafast time domain. Kamat and Patrick have carried out picosecond laser flash photolysis measurements on ZnO colloids in ethanol and have shown broad absorption in the near IR region and attributed to trapped electrons appearing within 20 ps. \textsuperscript{41} Caveleri \textit{et al} have shown with their measurements that the charge carriers fast and are size independent by 50 ps.\textsuperscript{42}

Femtosecond transient absorption measurements on ZnO nanomaterials by Bauer \textit{et al} have shown that the photo-generated charge carriers get trapped to around 60 meV below the conduction band edge by either radiative or non-radiative pathways.\textsuperscript{43} The UV emission was also studied by time-resolved spectroscopy for larger ZnO nanoparticles of 200 nm, ZnO nanowires, ZnO nanorods, ZnO nano needles and many other systems. The lifetimes of these larger nanoparticles and architectures are mostly bi-exponential with lifetimes of 70 ps and 350 to 116 ps to 1.2 ns. However, the lifetimes on these clusters were not monitored with faster time-resolved techniques with a time resolution of 200 fs and the reports used either streak camera or time-correlated single photon counting techniques with time resolution mainly is picoseconds to tens of picoseconds. To understand the dynamics of trapping and follow the lifetimes of smaller nanoparticles, faster
instrument response at least in the range of sub picoseconds are necessary.\textsuperscript{44-45} Direct band recombination times were reported by some groups to be in picosecond time domains.\textsuperscript{46-48} However, there is no systematic study that is present to probe the band edge luminescence dynamics in ZnO nanoparticles. Two things that can influence the luminescence lifetimes in quantum sized semiconductor nanoparticles: size of the nanoparticle as well as surface defects. As the size is increased, lifetime can be influenced by either trapping or inherent increase in the density of states in the conduction band. It is important to understand the dynamics of the charge carriers to gain insights into these parameters and such studies are crucial to determine their use in optical applications.

This investigation was carried out to probe the band edge luminescence dynamics of ZnO nanoparticles with an aim to differentiate the role of size versus trapping dynamics on charge carrier relaxation dynamics. (Scheme 3.1) To accomplish this objective, quantum-sized ZnO nanoparticles were synthesized by hydrolysis of zinc acetate with different chemical procedures that produced different sized ZnO nanoparticles. The band edge luminescence dynamics of different sized ZnO was followed with femtosecond fluorescence up-conversion spectroscopy after excitation at 266 nm. From the results, interesting trends were observed with regards to size and trap states.
Figure 3.1 Cartoon diagram depicting the main objective of the investigation that was to show the influence of the size and rate of trapping on band edge luminescence dynamics

3.2. Materials

Zinc acetate dihydrate, sodium hydroxide, lithium hydroxide, tetramethyl ammonium hydroxide hydrate, 2-propanol, absolute ethanol, dimethylsulfoxide were purchased from VWR and were used as received. Three methods were used to synthesize ZnO nanoparticles.

3.2.1. ZnO Synthesis in 2-propanol

The synthesis of ZnO in 2-propanol was adopted from the synthetic methodology developed by Spanhel and Anderson. For this synthesis, 0.1089 grams of zinc acetate was dissolved in 250 mL of 2-propanol by vigorous stirring. The 2 mM zinc acetate solution was then chilled to 0°C. Afterwards, 20 mL of a 0.02 M stock solution of sodium hydroxide was cooled to 0°C and added dropwise to the zinc acetate solution under vigorous stirring. The reaction solution was then removed and placed in a 55°C water bath. Here the reaction was set for two hours. ZnO nanoparticles formed immediately with the addition of the sodium hydroxide solution. Different sized ZnO nanoparticles were obtained by removing the sol from water bath at different time.
intervals. The measurements were carried out immediately after removing the sol from water bath. The sizes of ZnO were monitored by following the absorption onset.

3.2.2. ZnO Synthesis in Ethanol

The synthesis of ZnO was adopted from the work of Meulenkamp. Briefly, Zinc acetate dihydrate, 1.10 grams, was dissolved in 50 milliliters of ethanol in a hot water bath at 80°C and cooled to 0°C while at a vigorous stir. A 50 milliliter solution of 0.29 grams lithium hydroxide monohydrate was dissolved in ethanol by ultrasonication then cooled to 0°C. The lithium hydroxide monohydrate was added dropwise to the zinc acetate monohydrate and the reaction was set for two hours in hot water bath at 60°C. A heptane/hexane mixture was added to the solution to precipitate zinc oxide which was then centrifuged (3500 rpm). After centrifugation precipitate was re-dissolved in ethanol and in DMSO.

3.2.3. ZnO Synthesis in DMSO

The synthesis of ZnO in DMSO was adopted from the synthetic methodology described by Gamelin and co-workers. Briefly, two grams of zinc acetate dihydrate was dissolved in 90 milliliters of dimethylsulfoxide (DMSO) to make a 0.101M solution. Tetramethylammonium hydroxide hydrate was dissolved in 30 milliliters of ethanol to make a 0.552M solution which was added dropwise to the zinc acetate dihydrate solution under vigorous stirring.

3.3. Methods

Optical absorption measurements were carried out in Shimadzu UV-2102PC spectrophotometer. An Edinburgh F900 spectrofluorimeter was used to carry out steady-state luminescence measurements of ZnO. Time-resolved luminescence measurements of ZnO nanoparticles were studied using the newly set femtosecond luminescence up-conversion spectroscopic technique briefly described elsewhere. The upconversion system used in our
experiments was obtained from CDP Instruments, Inc., Russia. Specifically, the system used third harmonic generation from the mode-locked broad band Ti-sapphire laser (Spectra Physics, Tsunami, 710 to 920 nm). The present measurements were carried out with 280 nm excitation (the fundamental of Ti:sapphire was set at 840 nm). Polarization of the excitation beam for the magic angle luminescence and anisotropy measurements was controlled using a Berek compensator and the sample was continuously rotated with a rotating cell of 1 mm thickness. Horizontally polarized luminescence emitted from the sample was up-converted in a nonlinear crystal of $\beta$-barium borate using a pump beam at 800 nm, which first passed through a variable delay line. Instrument response function (IRF) was measured using the rise time of several dye molecules. Fitting the rise time of the luminescence traces gave a sigma value of ~290 fs. Parallel and perpendicular decay traces were obtained from which the magic angle luminescence decay was calculated from these traces. Fitting of the luminescence decay traces were carried out with DecFit software. Spectral resolution was achieved using a double monochromator and photomultiplier tube. The excitation average power varied, but was around $10 \pm 0.3$ mW. No degradation of the sample was observed as the traces overlapped after each repetition.

3.4. Results and Discussion

3.4.1. Optical Absorption and Steady-state Luminescence Measurements

The nanoparticles that were synthesized are characterized by optical absorption and steady-state luminescence measurements. It was shown by Meulenkamp that the size calculated from optical absorption measurements match well with the size determined from Brus’s equation as well as the size obtained from TEM measurements. Since the size is dependent on the time it was taken out of the water bath, we took the optical absorption band edge as an estimate to calculate the size of the nanoparticle. The sizes were determined for all synthesized ZnO nanoparticles and for the
sake of clarity, optical absorption spectra at different times from water bath for ZnO nanoparticles synthesized in isopropanol are shown in Figure 3.1 A. It is quite evident from the figure that as the time delay is increased, the optical absorption onset has shifted to longer wavelengths indicating that the size of the nanoparticle is increasing.

Figure 3.2 (A) Optical absorption spectra of ZnO nanoparticles synthesized in isopropanol taken at different times. (B) Luminescence spectra of ZnO synthesized with isopropanol. Emission spectra recorded at regular intervals during the growth of ZnO nanoparticles in 2-propanol excited at 310 nm

From the onset of absorption, nanoparticle size can be calculated using the following equation derived by Brus, \(^1,2\)

\[
E^* \approx E_{\text{g bulk}} - \frac{\hbar^2\pi^2}{2r^2} \left( \frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right) - \frac{1.8e^2}{4\varepsilon_0 r} - \frac{0.124e^4}{\hbar^2(4\varepsilon_0 r)^2} \left( \frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right)^{-1}
\]

Equation 3.1

where \(E_{\text{g bulk}}\) is the bulk bandgap, \(\hbar\) is the Plank’s constant, \(r\) is the particle radius, \(m_e^*\) is the effective mass of the electrons, \(m_h^*\) is the effective mass of the hole, \(m_0\) is the free electron mass, \(e\) is the charge on an electron, \(\varepsilon_0\) is the permittivity of free space and \(\varepsilon\) is the relative permittivity.

Using the effective masses of electrons and holes for ZnO and using the equation 3.1, a curve was
generated and shown in Figure 3.2. From the onsets of absorption of synthesized ZnO nanoparticles (Figure 3.1A) and overlaying the same on the curve shown in Figure 3.2, sizes of ZnO nanoparticles were determined. The luminescence spectra shown in Figure 3.1B reveal a trend in the trap state luminescence relative to the size of the ZnO nanoparticles. A decrease in the trap state luminescence intensity can be seen as the size of the particle increases. This shift in the trap state is relative the oxygen vacancies and increase of defect states present in the bands. The band edge luminescence remains significantly low in intensity.

![Figure 3.3](image)

**Figure 3.3** Plot of onset of absorption from Brus calculation and quantum mechanical calculation as a function of diameter of ZnO. This plot was used to calculate the sizes of ZnO nanoparticles.

Optical absorption and steady-state luminescence measurements were carried out for ZnO nanoparticles synthesized using different methods and corresponding absorption and photoluminescence spectra are shown in Figure 3.3. It is observed from Figure 3.3 that all the synthetic methods yielded similar absorption spectra with onset around 350 nm (depending on the size of the particle). Also, all of them have shown band edge luminescence as well as trap state
luminescence. This result shows that the dynamics that we are probing is for ZnO nanoparticles although their trap state densities can be different.

![Graph showing optical absorption and steady-state luminescence spectra of ZnO nanoparticles synthesized using different methods.](image)

**Figure 3.4** Optical absorption and steady-state luminescence spectra of ZnO nanoparticles synthesized using different methods

### 3.4.2. Time-resolved Band Edge Luminescence Measurements

The central objective of the present investigation is to probe the dynamics of band edge luminescence. The dynamics of trap state luminescence has been well investigated by researchers. However, similar work on band edge luminescence was quite limited as it is difficult to monitor with conventional time-resolved techniques and needs femtosecond time resolution. In this study, we have used the power of luminescence upconversion spectroscopy to probe band edge luminescence dynamics. The measurements were carried out after excitation at 266 nm with the third harmonic of Ti:Sapphire laser and monitoring the band edge luminescence at 350 to 370 nm depending on the size of the nanoparticle. Shown in Figure 3.4 A are the luminescence decay traces for different sized ZnO nanoparticles in isopropanol. To obtain the emission decay lifetimes, the decay traces \( F(t) \) were fit using a three exponential function:
\[ F(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} + a_3 e^{-t/\tau_3} \quad \text{Equation 3.2} \]

where \( a_1, a_2 \) and \( a_3 \) are amplitudes and \( \tau_1, \tau_2 \) and \( \tau_3 \) are the corresponding lifetimes. Average electron injection (\( \tau_{av} \)) time constants were determined using the following equation:

\[ \tau_{av} = \frac{\sum_i a_i \tau_i}{\sum_i a_i} \quad \text{Equation 3.3} \]

Lifetimes for 3.26 \( \text{nm} \) sized ZnO were found to be 1.2 ps (12.5%), 8.5 ps (44.1%), 26.5 ps (43.4%) with an average lifetime of 15.4 ± 1.3 ps. On the other hand, lifetimes of 4.3 \( \text{nm} \) sized ZnO have increased to 5.8 ps (8.1%), 14.5 ps (35.5%), 65.0 ps (56.4%) with an average lifetime of 42.3 ± 3.3 ps. Likewise, lifetimes and average lifetimes were obtained for different sized ZnO nanoparticles and are provided in Table 3.1. The average lifetimes were plotted as a function of size and shown in Figure 3.4 B. It is quite evident from the figure and table that the average lifetime of ZnO has increased significantly with an increase in the particle size of ZnO. This is in line with the fact that the average lifetime of bulk ZnO is around 340 ps. Although size and lifetime has a good correlation, it is not clear if size alone is the reason for differences in lifetimes.
Figure 3.5 (A) Band edge luminescence decay traces obtained after excitation at 266 nm. All the decay traces were fit with exponential decay functions. (B) Plot of average lifetime as a function of nanoparticle size

Table 3.1 Luminescence decay lifetimes for ZnO in isopropanol

<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>Lifetimes ((\tau))</th>
<th>Lifetimes ((\tau_{av}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.26</td>
<td>1.2 ps (12.5%), 8.5 ps (44.1%), 26.5 ps (43.4%)</td>
<td>15.4 ± 1.3 ps</td>
</tr>
<tr>
<td>3.4</td>
<td>1.2 ps (8.9%), 10.5 ps (50.0%), 32.5 ps (41.1%)</td>
<td>18.7 ± 1.6 ps</td>
</tr>
<tr>
<td>3.6</td>
<td>1.2 ps (10.1%), 10.5 ps (49.8%), 39.5 ps (40.1%)</td>
<td>20.8 ± 2.5 ps</td>
</tr>
<tr>
<td>3.88</td>
<td>1.5 ps (15.8%), 11.5 ps (42.3%), 41.5 ps (41.8%)</td>
<td>22.4 ± 3.5 ps</td>
</tr>
<tr>
<td>4.03</td>
<td>1.5 ps (5.3%), 11.8 ps (49.5%), 49.5 ps (45.2%)</td>
<td>28.2 ± 2.1 ps</td>
</tr>
<tr>
<td>4.07</td>
<td>1.5 ps (7.6%), 13.5 ps (46.0%), 49.8 ps (46.4%)</td>
<td>29.4 ± 2.3 ps</td>
</tr>
<tr>
<td>4.17</td>
<td>4.5 ps (6.9%), 12.8 ps (37.7%), 54.5 ps (55.4%)</td>
<td>35.3 ± 3.5 ps</td>
</tr>
<tr>
<td>4.3</td>
<td>5.5 ps (3.8%), 14.2 ps (44.7%), 63.5 ps (51.5%)</td>
<td>39.3 ± 3.2 ps</td>
</tr>
<tr>
<td>4.33</td>
<td>5.8 ps (8.1%), 14.5 ps (35.5%), 65.0 ps (56.4%)</td>
<td>42.3 ± 3.3 ps</td>
</tr>
</tbody>
</table>

To address the issue of size versus trapping dynamics, luminescence decay traces were monitored for ZnO synthesized using other methods, with LiOH as the base in the case of ZnO synthesized in ethanol. Shown in Figure 3.5A are the luminescence decay traces of different sized ZnO nanoparticles in ethanol after excitation at 266 nm and monitoring the respective band edge luminescence maxima. Note that the sizes of nanoparticles were obtained from the band edge absorption onset and correlating with the Brus relationship. It is observed from Figure 3.5A that the luminescence decay shows multi-exponential decay components and was fitted with a three exponential function and average lifetimes were determined from the analysis using Equation 3.3. Corresponding luminescence decay lifetimes are provided on Table 3.2 and the average lifetime versus size is plotted in Figure 3.5B. It is observed from the figure that the lifetime has again increased with increase in the size of ZnO as observed in the case of ethanol. It is observed from the table that the average lifetimes of ZnO in ethanol have ranged from 9.3 to 29.6 ps as the sizes
increased from 3.25 to 4.3. Compared to ZnO/IpOH, the ZnO nanoparticles prepared in ethanol displayed faster lifetimes.

Figure 3.6. Band edge luminescence decay traces obtained for ZnO prepared in the ethanol after excitation at 266 nm. All the decay traces were fitted with exponential decay functions.

<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>Lifetimes (τ)</th>
<th>Lifetimes (τ&lt;sub&gt;av&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.25</td>
<td>0.8 ps(22.5%), 5.2 ps(38.8%), 22.5 ps (38.7%)</td>
<td>10.9 ± 0.9 ps</td>
</tr>
<tr>
<td>3.36</td>
<td>1.2 ps(22.8%), 7.5 ps (31.7%), 27.5 ps(45.5%)</td>
<td>15.2 ± 1.5 ps</td>
</tr>
<tr>
<td>3.8</td>
<td>6.7 ps(35.8%), 36.8 ps (63.8%), 0.9 ps(0.4%)</td>
<td>25.9 ± 2.3 ps</td>
</tr>
<tr>
<td>4.0</td>
<td>3.0 ps(18.6%), 16.3 ps(29.4%), 48.5 ps(52.0%)</td>
<td>30.6 ± 2.3 ps</td>
</tr>
<tr>
<td>4.3</td>
<td>3.2 ps(7.2%), 11.8 ps(47.2%), 52.3 ps(45.5%)</td>
<td>29.6 ± 2.5 ps</td>
</tr>
</tbody>
</table>

Further luminescence decay measurements were carried on ZnO samples synthesized in DMSO with NH<sub>4</sub>OH as the base. Shown in Figure 3.6 are the corresponding luminescence decay traces for two different-sized ZnO nanoparticles of 3.6 and 3.9 nm after excitation at 266 nm and monitoring emission at 360 nm. The luminescence decays were fitted with multi exponential time constants and average lifetimes of 1.3 ps (for 3.6 nm) and 3.5 ps (for 3.9 nm) were obtained from...
the analysis. The trend in lifetimes is similar to ZnO synthesized in ethanol and isopropanol, but the lifetimes in DMSO are very short compared to the other results.

![Figure 3.7 Band edge luminescence decay traces for ZnO DMSO obtained after excitation at 266 nm. All the decay traces were fit with exponential decay functions.](image)

**Figure 3.7** Band edge luminescence decay traces for ZnO DMSO obtained after excitation at 266 nm. All the decay traces were fit with exponential decay functions.

Overall, luminescence decay lifetime analysis of ZnO synthesized with different methods have shown two main things. Firstly, the lifetimes increased with an increase in the size of the nanoparticle. Secondly, the lifetimes for ZnO in DMSO were significantly faster than ZnO in other solvents. As a comparison, the lifetimes of same sized ZnO nanoparticles synthesized using different methods were shown in Figure 3.7A. For a size of 3.9 nm, the luminescence decay of ZnO in DMSO is significantly faster than that of ZnO in EtOH and IpOH. To comprehend the results better, the average lifetimes of all ZnO were plotted as a function of size and shown in Figure 3.7 B. The lifetimes of ZnO in EtOH and IpOH seems to follow one trend while the lifetimes in DMSO have shown completely different trend. The results did not show a good trend for lifetimes with the size of nanoparticle.
Figure 3.8 (A) The intensity values of 3.9 nm sized particles plotted by the corresponding lifetime values. Average lifetimes plotted against the diameter of the different nanoparticle systems.

Other parameters that can influence the lifetimes of ZnO nanoparticle is the trapping dynamics wherein the excited electron or hole gets trapped into the surface defect states. A schematic in Figure 3.11 displays an idea of defects states present in the different ZnO nanoparticles system prepared in with different synthetical procedures. The trapping dynamics can be rationalized based on the intensity of band edge luminescence versus trap-state luminescence. With faster rate of trapping, band edge luminescence intensity would be lower while trap state luminescence intensity would be higher. Based on the ratio of trap-state to band-edge luminescence intensity ratios, it is possible to understand the effect of trapping on lifetimes. In an effort to probe the effect of trapping on the band edge luminescence dynamics, intensity ratios were determined for different sized ZnO synthesizes in different methods. For the sake of clarity of presentation, luminescence spectra of ZnO synthesized in EtOH, IpOH and DMSO were shown in Figure 3.8 A for 3.9 nm sized nanoparticle. It can be observed from the figure that the intensity ratio was highest for EtOH sample followed by IpOH and lowest for DMSO. This result suggests that the rate of trapping is faster for DMSO while it is slow for EtOH and IpOH. Further average
lifetimes of all ZnO nanoparticles synthesized in different methods were plotted as a function of intensity ratios and shown in Figure 3.8 B. There is a good correlation here suggesting that the rate of trapping dominates the band edge relaxation dynamics.

![Figure 3.9](image)

**Figure 3.9** (A) Luminescence spectra of 3.9 nm ZnO synthesized in different methods. (B) Plot of average lifetime versus the trap state to band edge luminescence intensity ratio.

Overall, the dynamics of band edge luminescence seems to be affected by the size. But, the size alone was unable to correctly provide the real picture of charge carrier relaxation dynamics. Rather it is the influence of trap states that dominates the band edge luminescence dynamics wherein the decrease in surface state densities thereby slowing down the trapping explains the slower lifetimes for larger sized ZnO nanoparticles. A comparison of lifetimes of ZnO synthesized in different methods followed the trend of trapping rather than the size alone. Thus, the dynamics of charge carriers can be explained using Figure 3.9. On band edge excitation, charges get relaxed to band edges to give rise to band edge luminescence. With time, both electrons and holes get trapped by shallow and deep trap states. The trap state luminescence arises from the recombination of these electrons and holes. This rate of trapping dominates the charge carrier relaxation dynamics in ZnO.
Figure 3.10 Schematic diagram depicting the charge carrier relaxation dynamics in ZnO nanoparticles

Figure 3.11. Schematic diagram depicting the idea of defect states present within different ZnO nanoparticle systems prepared with different synthetical procedures. (A) ZnO with no defect states B) ZnO prepared in alcohols IpOH and EtOH possess less defect-states C) more are present in ZnO prepared in DMSO ( V$_O$ represents the defect-states)
3.5. Conclusion

The main objective of the study is to understand the influence of the size on the charge carrier relaxation dynamics of band edge luminescence dynamics in bare ZnO nanoparticles. The investigations of the luminescence dynamics has implications in their optical applications of catalysis, sensing, and light harvesting. In the case of bare ZnO nanoparticles, both surface defect states as well as size can influence the band edge luminescence dynamics. To understand which pathway dominates the band edge luminescence dynamics, measurements were carried out on ZnO nanoparticles synthesized in different methods. Three different methods for synthesizing ZnO were used. They were ZnO in IpOH (NaOH as the base), ZnO in EtOH (LiOH as the base) and ZnO in DMSO (NH₄OH the base). All the synthetic methods were able to give different sized ZnO nanoparticles and the sizes were determined from the onset of absorption correlating it to Brus relationship. All ZnO nanoparticles have shown band edge luminescence as well as trap state luminescence that was expected as the ZnO nanoparticles were not passivated. The band edge luminescence dynamics was monitored for the first time for ZnO nanoparticles that was possible from luminescence upconversion technique with 266 nm excitation. The luminescence decay traces were fitted with multi-exponential decay components and average lifetimes were obtained. The average lifetimes with size have shown that as the size is increased, the lifetimes have increased. However, the ZnO in DMSO has shown significantly faster lifetime with same size nanoparticle and thus size alone was unable to explain the charge carrier dynamics. To comprehend better, a figure of merit for understanding the rate of trapping was realized from the intensity of trap state to band edge luminescence. There is a good correlation between the average lifetimes and the intensity ratio suggesting that the rate of trapping dominates the band edge luminescence dynamics in ZnO nanoparticles.
3.6. Summary of Chapter 3

- Band edge luminescence in ZnO nanoparticles was investigated to see if the size or surface state trapping has an effect on its charge carrier relaxation dynamics.

- Three different synthetical procedures were done to give a variety of possible surface defects and sizes for ZnO nanoparticles: in IpOH with sodium hydroxide; in EtOH with lithium mono hydroxide; and in DMSO with tetramethylammonium hydroxide.

- Ultrafast band edge luminescence dynamics of ZnO nanoparticles was investigated with third harmonic generation using 266 nanometer excitation to monitor the charge carrier dynamics via band edge luminescence dynamics.

- The luminescence lifetime measurements have shown that with increase in the size of the nanoparticle, the lifetimes have increased. However, the average lifetimes of different sized ZnO nanoparticles synthesized in different solvents did not match with size alone.

- The comparison of luminescence decays of the same size nanoparticles from each synthetical procedures shows that the surface defects and the rate of the trapping influences the band edge luminescence dynamics.

- The average lifetimes plotted against the ratio of trap state to band edge luminescence seem to match well suggesting the dominant role of surface trapping on charge carrier luminescence dynamics in bare ZnO nanoparticles.
3.7. References


CHAPTER 4

ULTRAFAST CHARGE CARRIER DYNAMICS IN CATECHOL AND SALICYLIC ACID DERIVATIVES MODIFIED TiO$_2$ NANOPARTICLES

4.1. Introduction

In the previous chapter, charge carrier dynamics of bare ZnO nanoparticles was studied. In this chapter, charge carrier dynamics in surface charge-transfer modified TiO$_2$ nanoparticles was investigated. Small molecules such as catechol and salicylic acid form charge-transfer complex with the surface of TiO$_2$ thereby creating new surface states in the band gap of TiO$_2$. Due to surface charge-transfer states, (Figure 4.1) the charge carrier dynamics will be significantly modified when compared to bare semiconductor nanoparticles. In addition, the dynamics of charge carriers in such surface modified semiconductor systems hold promise for applications in solar cells, catalysis and nonlinear optical materials.

![Figure 4.1 Schematic diagram of surface charge-transfer (CT) modified TiO$_2$ nanoparticles](image)

**Figure 4.1** Schematic diagram of surface charge-transfer (CT) modified TiO$_2$ nanoparticles
Charge-carrier relaxation dynamics in semiconductor nanoparticles has been actively investigated for last thirty years for their applications in photocatalysis, solar cells, light emitting displays etc. Among many semiconductor materials, most studied one is TiO$_2$ because of its excellent photo-stability, earth abundance, non-toxicity and inertness to chemical environments. For all these reasons, TiO$_2$ nanomaterials have found applications in photocatalysis, water splitting and solar fuels. Thus, the charge-carrier dynamics in bare TiO$_2$ nanoparticles has been the central focus of research groups. For applications in photocatalysis and solar cells, electron-hole recombination should be slower. Rothenberger et al$^1$ have studied the charge carrier trapping and recombination dynamics in 12 nm sized TiO$_2$ nanoparticles using laser flash photolysis. They have observed fast electron trapping on Ti$^{4+}$ states and nanosecond relaxation of trapped charge carriers. TiO$_2$ is an indirect band gap semiconductor and its luminescence quantum efficiency is negligible. So, most charge carrier dynamics investigations on TiO$_2$ nanoparticles were carried out with transient absorption measurements. Serpone and co-workers$^2$ have investigated the relaxation dynamics in TiO$_2$ sols and shown that electrons get trapped at surface states in less than 2 ps. Yang et al$^3$ have studied femtosecond charge carrier relaxation in TiO$_2$ colloids and have shown ultrafast electron and hole trapping.

Most charge carrier relaxation measurements on TiO$_2$ nanoparticles were carried out on bare particles that have very low visible absorption. To enhance the visible absorption, metal doping or surface modifiers are used. Ramakrishna and Ghosh$^4$ have synthesized dodecylbenzene sulfonate (DBS) capped TiO$_2$ nanoparticles and have shown unique visible luminescence and the surface modifier created surface states that lead to new luminescence. With surface modification, charge recombination also became slower. However, DBS type surfactants cannot really enhance visible light absorption as they are weakly coupled with TiO$_2$. It was shown by several researchers
that small molecules with ene-diol of ene-carboxyl and alcohol functional groups can form chelate charge-transfer (CT) complexes with surface defects of TiO$_2$ nanoparticles and enhance visible light absorption. Moser et al$^5$ have shown that catechol type molecules form charge-transfer complexes with TiO$_2$. Later on Rajh and co-workers$^6$ have shown that catechol surface modified TiO$_2$ nanoparticles can be able to enhance Raman signals of nearby molecules similar to that of surface-enhanced Raman scattering. Significant experimental and theoretical efforts were focused on understanding the type of excitations in these surface-modified nanoparticles. Lian and co-workers$^7$ have studied the dynamics of interfacial charge-transfer in catecholate derivative-sensitized TiO$_2$ nanoparticles and have shown that charge-transfer can be modeled by Marcus electron transfer theory. In a recent study, Varaganti and Ramakrishna$^8$ have shown the CT complexation with catechol, salicylic acid, hydroxamic acid and acetylacetonate with TiO$_2$ nanoparticles and shown ultrafast luminescence from such complexes. Theoretical calculations have shown that these CT excitations are localized. However, it was shown with ultrafast luminescence anisotropy measurements that these excitations are localized early and gets delocalized into the conduction band of TiO$_2$ quickly. But, the effect of donor/acceptor strength on charge-carrier relaxation is not quite understood and such information can help design better materials for optical applications. Also, surface morphology can play a vital role in the charge carrier dynamics and such measurements were limited.

To address these concerns, this study was carried out. To understand the effect of donor/acceptor strength on the charge-carrier relaxation dynamics, measurements were carried out on several catechol derivatives and salicylic acid derivatives. The molecular structures of the investigated small molecule derivatives are shown in Figure 4.2. Both donors and acceptors were studied for catechol while an amine donor was investigated for salicylic acid. To probe the effect
of morphology on charge carrier relaxation dynamics, measurements on TiO$_2$ nanoparticles in solution and TiO$_2$ thin films were carried out. Thin film structures of TiO$_2$ possess lower trap state density compared to nanoparticles in solution. Femtosecond luminescence and transient absorption measurements were carried out in solution and in thin films out to understand the charge injection and charge separation dynamics.

![Molecular structures of the investigated small molecule derivatives](image)

**Figure 4.2** Molecular structures of the investigated small molecule derivatives

4.2. Experimental

4.2.1. Materials

Catechol, MetCat, CN-Cat, NO$_2$-Cat, NH$_2$-Sal, Sal, and Titanium (IV) tetraisopropoxide were obtained from Sigma-Aldrich and were used as such. Methanol and isopropanol were
obtained from Sigma-Aldrich and were used as received. Nanopure water was used to make all the samples unless otherwise stated. TiO$_2$ nanopaste was obtained from Solaronix, inc.

### 4.2.2. Synthesis of TiO$_2$ Nanoparticles

TiO$_2$ nanoparticles were synthesized using sol-gel process described elsewhere.$^{9,10}$ Briefly, TiO$_2$ nanoparticles were synthesized by the controlled hydrolysis of titanium (IV) tetraisopropoxide. 10 mL of Ti[OCH(CH$_3$)$_2$)$_4$ was dissolved in 90 mL of isopropyl alcohol and was added drop wise at a rate of 1 mL min$^{-1}$ to 900 mL nanopure water (pH 1.5) at 275 K with continuous stirring that persisted for 12 h. A transparent colloid was formed which was concentrated at 308-313 K with a rotary evaporator. The resulting powder was then dried under nitrogen to yield a white powder. TiO$_2$ films were made using the doctor-block method.$^{11}$ ITO glass slides were cut into squares using a diamond cutter, washed and blow dried. Doctor blading was carried out on the conducting side of 10 Ω ITO coated glass slides. The films were allowed to dry for 5 minutes at room temperature after which they were placed in an oven for 45 minutes at 723 K. They were then taken out and allowed to cool down to room temperatures before being immersed in the appropriate small molecule solution for 30 minutes. They were then taken out and washed with methanol to remove any nonadsorbed small molecules.

### 4.2.3. Methods

Optical absorption measurements were carried out using Shimadzu UV 2101 PC absorption spectrometer. Benesi-Hildebrand analysis was used to determine the association constants which will be discussed in the main text. Time-resolved fluorescence and fluorescence anisotropy of molecule-TiO$_2$ nanoparticles were studied using the femtosecond fluorescence upconversion described elsewhere.$^{12}$ The upconversion system used in our experiments was obtained from CDP systems, and the design is similar to what has been published earlier.$^{12}$ Specifically, the system
used frequency doubled (400 nm) light from a mode-locked broadband Ti-sapphire laser (Spectra Physics, Tsunami, 710-920 nm). The sample was continuously rotated with a rotating cell which is 1 mm thick to avoid the degradation of the sample. Horizontally polarized fluorescence emitted from the sample was upconverted in a nonlinear crystal of -barium borate using a pump beam at 800 nm, which was passed through a variable delay line. Instrument response function (IRF) was measured using Raman scattering from water. Fitting the Gaussian peak from the Raman scattering yielded a sigma value of \(\sim 130\) fs which gave a full width half maximum of \(\sim 250\) fs. Spectral resolution was achieved by using a double monochromator and photomultiplier tube. The excitation average power varied during experiments but was mostly in the range of 21 ± 0.5 mW. Time-resolved fluorescence anisotropy (r(t)) measurements were carried out with parallel and perpendicular excitations whose polarization was changed with a Berek compensator. Fluorescence anisotropy was calculated from the traces obtained from the parallel and perpendicular excitation using a method\(^{13, 14}\) which is based on the ratio of difference between parallel and perpendicular polarized emissions over magic-angle fluorescence.

Femtosecond transient absorption investigations were carried out using an ultrafast pump-probe spectrometer detecting in the visible region located at Argonne National Laboratory and is exhaustively described elsewhere.\(^{15-17}\) Briefly, 1 mJ, 100 fs pulses at 800 nm with a repetition rate of 1 KHz were obtained from a Nd:YLF (Empower) pumped Ti:sapphire regenerative amplifier (Spitfire, Spectra-Physics) with the input from Millennia pumped Ti: sapphire oscillator (Spectraphysics, Tsunami). The output of laser beam was split to generate pump and probe beam pulses with a beam splitter (85% and 15%). The pump beam was produced by an optical parametric amplifier. The pump beam used in the present investigation, i.e., 420 nm, was obtained from the fourth harmonic of the idler beam. The probe beam was delayed with a computer-controlled
motion controller and then focused into a 2 mm sapphire plate to generate white light continuum. The white light was then overlapped with the pump beam in a 2 mm quartz cuvette containing the sample, and the change in absorbance for the signal was collected by a CCD detector (Ocean optics). Data acquisition was controlled by the software from Ultrafast systems inc. Typical power of the probe beam was around 10 µJ/cm² while the pump beam was around 1000 µJ/cm². Magic angle polarization was maintained between the pump and probe using a wave plate. The pulse duration was obtained from the non-resonant fitting of the solvent response, which was around 130 fs. The samples were stirred by a rotating magnetic stirrer and little degradation of the sample was observed during the experiments. Blank experiments were carried out with bare TiO₂ nanoparticles, and water and minimal signal was observed, as they do not possess absorption at the excitation wavelength of 420 nm.

4.3. Results and Discussion

4.3.1. Optical Absorption Measurements

Molecules with ene-diol functional groups bind strongly with TiO₂ nanoparticles via the formation of a ligand to metal charge-transfer (LMCT) complex. Theoretical calculations have shown that the highest occupied molecular orbital (HOMO) is located on the catecholate molecule and the lowest un-occupied molecular orbital (LUMO) located on the Ti metal atom. This gives rise to its broad absorption in the visible region centered around 400 nm. Optical absorption measurements were carried out on all the catechol derivative-functionalized TiO₂ and salicylic acid derivative-functionalized TiO₂ and are shown in parts A and B Figure 4.3, respectively. It was observed from Figure 4.3 that all small molecules form strong LMCT complexes with the surface of TiO₂ nanoparticles and thereby modifying its surface. The results are consistent with what has been reported in the literature. With catechol derivatives, absorption onset of TiO₂ has shifted
close to 600 nm (Figure 4.3A) while with salicylic acid derivatives, absorption onset only shifted to 520 nm. In addition, with increasing the acceptor strength in catechol derivatives, the absorption maximum of LMCT complexes is shifted to longer wavelengths suggesting a strong complex with TiO$_2$. However, no such shift is observed with salicylic acid derivatives.

**Figure 4.3** Optical absorption spectra of (A) catechol derivatives functionalized TiO$_2$ and (B) Salicylic acid derivatives functionalized TiO$_2$. Also shown for comparison in the absorption spectrum of bare TiO$_2$ nanoparticles in solution. Note the shift in absorption onset confirming the surface modification.

### 4.3.2. Association Constants of Molecule/TiO$_2$ Nanoparticles: Benesi-Hildebrand Analysis

The association constants of the catecholate derivative molecule/TiO$_2$ complexes were determined from Benesi-Hildebrand plots.\(^49\) The Benesi-Hildebrand analysis works with the assumption that there is a 1:1 complexation between the molecules to surface Ti atoms. Equilibrium in the molecule /TiO$_2$ complexes can be concisely expressed as:

$$Ti_{surf} + RH_2 \xrightarrow{K_a} Ti - R$$  \(\text{Equation 4.1}\)
where, $T_i_{surf}$ represents the surface Ti atoms, $RH_2$ the molecule, $Ti - R$ the charge transfer complex formed between Ti and molecule and $K_a$ is the equilibrium constant. From equation (4.1), $K_a$ can be expressed as,

$$K_a = \frac{[Ti-R]}{[Ti_{surf}][RH_2]}$$

Equation 4.2

Since $Ti_{surf}$ is directly proportional to TiO$_2$ concentration ($C_{TiO_2}^0$), $K_a$ can be rewritten as:

$$K_a = \frac{C_{Ti-R}}{(C_{TiO_2}^0 - C_{Ti-R})(C_{RH_2}^0 - C_{Ti-R})}$$

Equation 4.3

where $C_{RH_2}^0$ is the initial concentration of the molecule. Assuming $C_{RH_2}^0 \gg C_{Ti-R}$, equation (4.3) can be re-expressed as:

$$\frac{C_{TiO_2}^0}{A} = \frac{1}{K_a \varepsilon l} \frac{1}{C_{RH_2}^0} + \frac{1}{\varepsilon l}$$

Equation 4.4

where $\varepsilon$, and $l$ are the extinction coefficient and the path length of the cuvette, respectively. A plot of $\frac{1}{A}$ against $\frac{1}{C_{RH_2}^0}$ yielded a line with a slope of $\frac{1}{C_{TiO_2}^0 K_a \varepsilon}$ and an intercept of $\frac{1}{C_{TiO_2}^0 \varepsilon}$. Following equation (4.4) association constants were determined at different wavelengths and averaged values presented.

Absorption spectra as a function of small molecule concentration were shown in parts A and B of Figure 4.4 for MetCat and NO$_2$-Cat, respectively. Corresponding BH plots are shown in the insets of figures. The Associations constants were determined for all small molecules similarly and provided in Table 4.1. It can be observed from Table that increasing the acceptor strength increase the association constant for catechol derivatives/TiO$_2$ nanoparticles. The results confirm that molecules with an acceptor group form stronger CT complex with the surface of TiO$_2$ (deeper potential well) compared to molecule with a donor group (MetCat). This result has consequences
in charge-carrier dynamics. To understand charge carrier relaxation dynamics, femtosecond luminescence and absorption measurements were carried out.

Figure 4.4 Benesi-Hildebrand analysis of TiO$_2$/molecule charge-transfer complexes for (a) MetCat and (b) NO$_2$-Cat. It can be observed that there is one order of magnitude difference in the association constants with different substitution on the catechol.

Table 4.1 Association constants determined from Benesi-Hildebrand Analysis

<table>
<thead>
<tr>
<th>Molecule/TiO$_2$</th>
<th>Association Constant $K_a$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat/TiO$_2$</td>
<td>8.8 ± 0.8 x 10$^3$</td>
</tr>
<tr>
<td>MetCat/TiO$_2$</td>
<td>1.2 ± 0.4 x 10$^3$</td>
</tr>
<tr>
<td>CN-Cat/TiO$_2$</td>
<td>1.1 ± 0.3 x 10$^4$</td>
</tr>
<tr>
<td>NO$_2$-Cat/TiO$_2$</td>
<td>2.0 ± 0.3 x 10$^4$</td>
</tr>
<tr>
<td>Sal/TiO$_2$</td>
<td>1.0 ± 0.2 x 10$^3$</td>
</tr>
<tr>
<td>NH$_2$-Sal/TiO$_2$</td>
<td>1.0 ± 0.5 x 10$^3$</td>
</tr>
</tbody>
</table>
4.3.3. Femtosecond Luminescence Measurements

In a previous investigation,\textsuperscript{8,51} our group researchers have shown ultrafast luminescence from catechol, salicylic acid, hydroxamic acid, acetylacetonate-functionalized TiO$_2$ nanoparticles, and have shown that the luminescence anisotropy can be used to demonstrate the localized/delocalized nature of the CT excitation. One important aspect is that both catechol and salicylic acid-functionalized TiO$_2$ show ultrafast luminescence decay and localized excitation. Before going further, the data obtained for the dynamics measurements of Cat/TiO$_2$ and Sal/TiO$_2$ are discussed. Shown in Figure 4.5A are the luminescence kinetic decay traces of Cat/TiO$_2$ at different emission wavelengths. It has to be mentioned here that free TiO$_2$ in water, or molecule-in-water, or water-alone do not give any luminescence signals at these wavelengths as the absorption is negligible. Thus, the luminescence arising out of Cat/TiO$_2$ systems are assigned to charge-transfer emission from molecule/TiO$_2$ nanocomposites. The decay traces are fit with <100 fs indicating ultrashort carrier recombination dynamics. However, this ultrafast luminescence can also be assigned to ultrafast delocalization of electron into the conduction band of TiO$_2$. Luminescence anisotropy measurements for Cat/TiO$_2$ show anisotropy close to 0.4 indicating that the luminescence is arising out of a localized charge-transfer state with a dipole aligned parallel to the excitation. (Figure 4.4B) The ultrafast decay thus can be attributed to charge delocalization into the conduction band of TiO$_2$. Similar measurements were carried out for Sal/TiO$_2$ (Figure 4.4C) and the kinetics also decayed with an ultrafast time constant followed by sub-picosecond decay component. Fluorescence anisotropy decay traces of Sal/TiO$_2$ (Figure 4.4D) also show localized excitation. However, the anisotropy of slower component present the delocalization dynamics. So, here again the decay of ICT luminescence is assigned to rate of charge delocalization into the conduction band of TiO$_2$. 
Figure 4.5 Fluorescence kinetic decay traces monitored for Cat/TiO$_2$ (A) at different emission wavelengths and corresponding anisotropy decay traces (B). Also shown are fluorescence kinetic decay traces at different emission wavelengths for (C) Sal/TiO$_2$ and corresponding anisotropy decay traces (D).

The fact that the majority of the decay is dominated by <100 fs suggests that the charge delocalization into TiO$_2$ isplace very fast. To further understand how the donor and acceptor substitution on catechol and salicylic acid influence the CT luminescence decay and the charge delocalization into the conduction band of TiO$_2$, ultrafast luminescence measurements were carried out with 400 nm excitation. For the clarity of the presentation in comparison of the sample,
the femtosecond luminescence decay traces of Cat, MetCat, NO$_2$-Cat and CN-Cat at a wavelength of 500 nm are shown in Figure 4.5 A. Also a comparison of charge-transfer emission decays for Sal and NH$_2$-Sal on TiO$_2$ nanoparticles are presented in Figure 4.5B.

**Figure 4.6** Femtosecond luminescence decay traces for different catechol derivatives on the surface of TiO$_2$ nanoparticles. (A) Similar luminescence kinetic decay comparison for Sal derivatives (B)

As observed in Cat/TiO$_2$ and Sal/TiO$_2$, luminescence kinetic decay traces of their derivatives also show ultrafast luminescence decay lifetimes followed by slower component. All the fluorescence kinetic decay traces were fit with two-exponential decay component with an instrument response limited lifetime followed by slower sub-picoseconds lifetime and corresponding time constants determined from the analysis are provided in Table 4.2.

**Table 4.2** Fluorescence lifetimes of the investigated small-molecule/TiO$_2$ nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lifetimes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat/TiO$_2$</td>
<td>$\tau_1 &lt; 100$ fs (99.6%), $\tau_2 = 500 \pm 80$ fs (0.4%)</td>
</tr>
</tbody>
</table>

95
It can be observed from Table 4.2 that the lifetime vary notably with NO$_2$-Cat/TiO$_2$ system having the slowest lifetime among them while MetCat/TiO$_2$ lifetime close to the instrument response. There is a trend in decay constants where in the acceptor substitution slightly increasing the decay time constants. However, with donors, the lifetime has become faster. The differences are arising probably from the different delocalization time constants. However, no such trend was observed in Sal derivatives.

NO$_2$-Cat is one derivative with greater acceptor strength. Wavelength dependent time-resolved luminescence measurements were carried out on NO$_2$-Cat functionalized TiO$_2$ to check if the slowing down of luminescence is accurate. Shown in Figure 4.6 A are the fluorescence kinetic decay traces of NO$_2$-Cat/TiO$_2$ at different emission wavelengths after excitation at 400 nm. It can be observed that the slow component is more apparent at higher emission wavelengths (Table 4.3) suggesting that the delocalization to the conduction band of TiO$_2$ is slower with an increase in emission wavelength. This is accurate for the following reasons: With increase in emission wavelength, we are probing the deeper potential well and the electron delocalization into the conduction band of TiO$_2$ will face an uphill energy barrier. Also shown are the anisotropy
decays that show consistently that the emission is arising out of the localized charge-transfer states (Figure 4.6B).

![Figure 4.7](image)

**Figure 4.7** Wavelength dependent luminescence decay traces NO$_2$-Cat/TiO$_2$ nanoarticles after excitation at 400 nm. (A) The anisotropy traces which show that the anisotropy is independent of emission wavelength and the excitation is fairly localized (B)

**Table 4.3** Fluorescence lifetimes at different wavelengths for NO$_2$-Cat/TiO$_2$ composites

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Lifetimes</th>
</tr>
</thead>
<tbody>
<tr>
<td>480 nm</td>
<td>$\tau_1&lt;100$ fs (99.4%), $\tau_2=500 \pm 100$ fs (0.6%)</td>
</tr>
<tr>
<td>500 nm</td>
<td>$\tau_1&lt;100$ fs (99.5%), $\tau_2=400 \pm 100$ fs (0.5%)</td>
</tr>
<tr>
<td>520 nm</td>
<td>$\tau_1&lt;100$ fs (97.5%), $\tau_2=500 \pm 100$ fs (2.5%)</td>
</tr>
<tr>
<td>550 nm</td>
<td>$\tau_1&lt;100$ fs (91.5%), $\tau_2=500 \pm 100$ fs (8.5%)</td>
</tr>
<tr>
<td>580 nm</td>
<td>$\tau_1&lt;100$ fs (90.6%), $\tau_2=700 \pm 100$ fs (9.4%)</td>
</tr>
<tr>
<td>610 nm</td>
<td>$\tau_1&lt;100$ fs (90.7%), $\tau_2=900 \pm 130$ fs (9.3%)</td>
</tr>
</tbody>
</table>
From the luminescence upconversion measurements, it was determined that the charge-transfer luminescence is localized for all molecule/TiO$_2$ nanocomposites and delocalization into the conduction band of TiO$_2$ dominates the relaxation dynamics. Interestingly, the delocalization into conduction band of TiO$_2$ is slower with increase in acceptor strength indicating that the acceptor substituted catechol derivatives prefer to stay in their localized states. Further femtosecond transient absorption measurements were carried out to probe the charge carrier relaxation dynamics.

4.3.4. Transient Absorption Measurements

Transient absorption measurements can probe not only the excited states of molecules but also probe the charge separated species such as cation radicals and electrons in the conduction band or trap states of TiO$_2$. As TiO$_2$ is an indirect bandgap semiconductor, most charge carrier dynamics studies were carried out using transient absorption only. Transient absorption measurements were also carried out for present systems to understand the nature of charge-transfer intermediates, charge separation and charge recombination. For the sake of control, transient absorption data for Cat/TiO$_2$ and Sal/TiO$_2$ are discussed first followed by their derivatives. Figure 4.7A shows the excited state absorption (ESA) at different time delays for Cat/TiO$_2$ after excitation at 420 nm. ESA at 150 fs time delay shows a maximum around 540 nm and a featureless absorption greater than 650 nm. In addition, bleach was observed below 470 nm. The bleach arises from the disappearance of charge-transfer absorption while the positive feature at 550 nm is assigned to the bound cation radical (Cat$^+$/Ti$^{3+}$) and the absorption at wavelengths greater than 650 nm is assigned to the absorption of conduction band electrons. It can be observed from Figure 4.7A that the bound Cat$^+$/Ti$^{3+}$ ESA decays as a function of time to give rise to a broader absorption centered around 600 nm and absorption greater than 650 nm. The ESA kinetics at 550 nm (Figure 4.7B)
decays faster than that of the kinetics at 675 nm (Figure 4.7C). However, one can observe the charge recombination from the decay of the transient at 675 nm. This is because of the fact that the kinetics at 550 nm overlaps both the decay of bound Cat$^+/Ti^{3+}$ and the conduction band electrons and thus decays faster than that of 675 nm kinetics. So, for the case of Cat/TiO$_2$, the charge injection takes place instantaneously as observed from the ESA greater than 650 nm (arises from the electrons in conduction band). However, the transients still possess the absorption of bound charge-transfer exciton (Cat$^+/Ti^{3+}$) that recombines or delocalizes to give rise to conduction band electrons. This ultrafast recombination of charge carriers in Cat/TiO$_2$ in solution phase is not ideal for solar cell and photo-catalytic applications.
Figure 4.8 (A) ESA spectra at different time delays for Cat/TiO$_2$ after excitation at 420 nm. Corresponding transient decay traces at (B) 550 nm and (C) 675 nm

Similar transient absorption measurements were carried out for Sal/TiO$_2$ nanoparticles in solution and shown in Figure 4.8A are the ESA at different time delays from 200 fs to 20 ps. The ESA at 200 fs possess both broad absorption at 500 nm and absorption greater than 650 nm. No bleach was observed as the absorption of the charge-transfer complex for Sal/TiO$_2$ is below the monitoring wavelength region. Both 505 nm (Figure 4.8B) as well as the absorption at 690 nm (Figure 4.9C) decay fairly rapidly. But, the decay at 505 nm decays little faster than that of 690 nm. However, faster components are observed for both cases and are assigned to charge recombination. In contrast to Cat/TiO$_2$, there is no different transient for Sal/TiO$_2$ that can be assigned to localized charge-transfer exciton. This is probably because Cat forms a CT complex with defect Ti$^{3+}$ more rapidly while Sal forms a complex with Ti$^{4+}$ sites. This is probably the reason for observing absence of a specific transient for the localized CT exciton for Sal/TiO$_2$ when compared to Cat/TiO$_2$. It is interesting to note differences in transient absorption features for Cat and Sal by themselves and probably the substituents can definitely influence their charge-carrier relaxation of surface modified TiO$_2$ further.
Figure 4.9 (A) ESA spectra at different time delays for Sal/TiO$_2$ after excitation at 420 nm. Corresponding transient decay traces at (B) 505 nm and (C) 690 nm.

Femtosecond fluorescence measurements have shown major differences between the CT luminescence decay for MetCat (donor substituted catechol) and NO$_2$-Cat (acceptor substituted catechol). Thus, ESA features of MetCat and NO$_2$-Cat are discussed in detail here. Shown in Figure 4.9A are the ESA at different time delays for MetCat/TiO$_2$ after excitation at 420 nm. Unlike Cat/TiO$_2$, the ESA features of MetCat/TiO$_2$ are quite different. The ESA at 150 fs time delay consists of a positive feature centered around 480 nm and another with a maximum at 650 nm overlapped with broad feature less absorption greater than 680 nm. The ESA maximum at 480 nm
is assigned to bound MetCat$^+/\text{Ti}^{3+}$ charge-transfer exciton and other features are assigned to the cation radical of MetCat and electron in the conduction band. The fact that the charge separated species are observed immediately after excitation suggest immediate delocalization of the excited charge carriers and matches fairly well with what was observed in femtosecond fluorescence upconversion measurements.

Figure 4.10 (A) ESA spectra at different time delays for MetCat/TiO$_2$ after excitation at 420 nm. Corresponding transient decay traces at (B) 480 nm and (C) 650 nm.
However, the bound CT exciton at 480 nm (Figure 4.9B) decays fast until that ESA vanishes. In contrast, the ESA at 650 nm (Figure 4.9C) does not decay fast. The results show that it is possible to achieve good charge separation with donor substituted catechol. Even though there is a contribution of bound CT exciton, charge separation greater than 50% was observed in this system. It would be interesting to see if acceptor substituted catechol can lead to similar charge separation. Figure 4.10A shows the ESA at different time delay for NO₂-Cat/TiO₂ after excitation at 420 nm.

**Figure 4.11** (A) ESA spectra at different time delays for NO₂-Cat/TiO₂ after excitation at 420 nm. Corresponding transient decay traces at (B) 480 nm and (C) 650 nm.
It can be observed from Figure 4.10A that the ESA at 150 fs consisted a positive feature centered around 540 nm. The transient features below 520 nm were complicated by the intense ground state absorption of NO$_2$-Cat/TiO$_2$. This ESA at 540 nm is assigned to the absorption of NO$_2$-Cat$^+/\text{Ti}^{3+}$ CT excitonic state. It is interesting to note the absence of ESA greater than 650 nm indicating that ultrafast charge separation is quite negligible for NO$_2$-Cat/TiO$_2$ system. Optical absorption and fluorescence upconversion measurements have shown that the localized CT state of NO$_2$-Cat and Ti$^{3+}$ defect states is very strong creating deeper trap state from where the delocalization into the conduction band of TiO$_2$ is difficult. However, as the time delay is increased, the bound CT excitonic state decays (Figure 4.10B) very fast and smaller charge separating species were formed. With time delay, there is a formation of transient greater than 650 nm suggesting the delocalization into the conduction band of TiO$_2$ from the bound localized CT state. Figure 4.10C shows a growth to form electron in the conduction band absorption, but its contribution is almost 10 to 20 times smaller than that of MetCat and Cat. Contrasting ESA features were observed for different substituents on catechol.

Similar transient absorption measurements were carried out for all derivatives. The features observed are fairly similar to what was discussed above. To avoid repetition, only the comparison of kinetics of different catechol derivatives at their respective ESA maxima is presented. Shown in Figure 4.11A are the comparison kinetics decay traces for Cat-derivatives on TiO$_2$ nanoparticles in solution. It can be observed from figure that the kinetics of MetCat decays quite slowly compared to that of CN-Cat and Nitro-Cat. The percent of long components in decay is shorter with increase in acceptor strength (Table 4.4). The results clearly show that the donor substitution
leads to better charge separation when compared to acceptor even though stronger CT complex is formed with an acceptor substitution.

**Figure 4.12** Comparison of kinetic decay at their ESA maxima for (A) Cat-derivatives/TiO$_2$ and (B) Sal derivatives/TiO$_2$

Figure 4.11B shows the comparison between the kinetic decay traces of Sal/TiO$_2$ and NH$_2$-Sal/TiO$_2$ in solution. Interestingly, not much of difference is observed between the kinetics and their lifetimes (Table 4.4) for Sal/TiO$_2$ and NH$_2$-Sal/TiO$_2$ pointing to the fact that Sal forms weaker complex with Ti$^{3+}$ than that of Ti$^{4+}$. As Sal forms a complex with Ti$^{4+}$, charge separation occurs immediately without the presence of intermediate localized CT excitonic state and thus no effect of substituent was observed.

**Table 4.4** Transient decay times of the investigated small molecule/TiO$_2$ nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lifetimes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat/TiO$_2$</td>
<td>$\tau_{av} = 1.7 \pm 0.3$ ps (85.1%), $\tau_{long} &gt; 30$ ps (14.9%)</td>
</tr>
<tr>
<td>MetCat/TiO$_2$</td>
<td>$\tau_{av} = 5.5 \pm 0.5$ ps (46.8%), $\tau_{long} &gt; 30$ ps (53.2%)</td>
</tr>
</tbody>
</table>
The transient absorption measurements have shown distinct differences between different substituents, especially for the case of Cat-derivatives. The hypothesis is that Cat forms CT complex with Ti$^{3+}$ defect sites and creates a localized CT excitonic state that was detrimental for achieving efficient charge separation. However, that effect was minimized by the use of a donor which gave decent charge separation even in solution phase. Thin films of TiO$_2$ possess much smaller defect states as they are heated to remove dangling bonds and the density of defect states are much smaller. It would be interesting to see if there are any differences in transient absorption features for Cat/TiO$_2$ in solution and thin film phases. The transient absorption features of Cat/TiO$_2$ in solution were already discussed above and the main result is the presence of ESA feature for bound Cat$^+$/Ti$^{3+}$ at 550 nm. Shown in Figure 4.12 A are the ESA at different time delays for Cat/TiO$_2$ thin films. It is quite interesting to see completely different features. The ESA for Cat/TiO$_2$ thin film at 200 fs is dominated by bleach with a maximum at 470 nm and broad featureless absorption greater than 650 nm. The bleach is due to the disappearance of Cat/TiO$_2$ absorption and the ESA greater than 650 nm is assigned to the absorption of electrons in the conduction band of TiO$_2$. This result proves our hypothesis that the absorption observed for Cat/TiO$_2$ in solution phase is that of the localized CT excitonic state. The transient decay traces at 650 nm were compared for Cat/TiO$_2$ in solution and thin film phases (Figure 4.12 B) and one can

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\tau_{av}$ (ps)</th>
<th>$\tau_{long}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN-Cat/TiO$_2$</td>
<td>0.65 ± 0.1</td>
<td>&gt;10</td>
</tr>
<tr>
<td>NO$_2$-Cat/TiO$_2$</td>
<td>2.7 ± 0.3</td>
<td>100</td>
</tr>
<tr>
<td>Sal/TiO$_2$</td>
<td>3.5 ± 0.3</td>
<td>&gt;10</td>
</tr>
<tr>
<td>NH$_2$-Sal/TiO$_2$</td>
<td>3.8 ± 0.4</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

Table 4.4 - continued
observe the absence of any charge recombination in thin film phases. This is one of the first results that shows the possibility of achieving long-lived charge separation with Cat/TiO$_2$ systems.

![Graph A: ESA spectra of Cat/TiO$_2$ thin film at different time delays](image)

**Figure 4.13** (A) ESA spectra of Cat/TiO$_2$ thin film at different time delays and (B) kinetic decay trace comparison for solution and thin film phases

Similar comparison of transient features was carried out for Sal/TiO$_2$ in solution and thin film phases. The transient features of Sal/TiO$_2$ in solution consisted of ESA maximum at 500 nm and broad absorption for electrons in the conduction band. Likewise, the ESA of Sal/TiO$_2$ thin film (Figure 4.13A) consisted of an ESA maximum at 500 nm, another shoulder at 630 nm and broad featureless absorption greater than 650 nm. The ESA features of Sal/TiO$_2$ in solution and thin film phases are more or less similar where in the excitation of complex leads to instantaneous charge separation with the formation of cation radical of sal and electrons in the conduction band. The kinetic decay traces were compared for solution and thin film phases and shown in Figure 4.13 B. There is a fast decay in both cases of solution and thin film. However, the charge separation is higher for thin film compared to solution. This is expected as the defect state densities are lower in thin film leading to better charge separation. Cat/TiO$_2$ has shown differences in the manner Cat
forms complex with Ti$^{3+}$. In the case of Sal, it forms a better complex with Ti$^{4+}$ in solution phase as well as thin films and thus no major differences in charge-carrier relaxation was observed in the case of Sal/TiO$_2$.

![Graph A](image1)

![Graph B](image2)

**Figure 4.14** (A) ESA spectra of Sal/TiO$_2$ thin film at different time delays and (B) kinetic decay trace comparison for solution and thin film phases.

### 4.4. Mechanism of Charge-Carrier Relaxation Dynamics in Surface-Modified TiO$_2$ Nanoparticles

Optical absorption, time-resolved fluorescence and absorption measurements carried out on catechol and salicylate derivatives have shown following things. Charge-transfer complexes were formed with all small molecule derivatives with TiO$_2$ nanoparticles in solution and all molecules were able to modify the surface of TiO$_2$ with catechol derivatives shifting the absorption to 600 nm while salicylate derivatives shifting to 520 nm. With increasing the acceptor strength of catechol, CT absorption was stronger and shifted to longer wavelengths with NO$_2$-Cat forming strongest complex. All the investigated small molecule derivatives have shown ultrafast ICT emission. The CT emission decay was mostly instrument response limited for catechol derivatives, and anisotropy measurements have shown that the emission arises out of localized CT states. With increasing the acceptor strength, the ICT emission decay slowed down with the NO$_2$-Cat/TiO$_2$
complex showing slowest decay. The ICT decay is attributed to the charge delocalization into the conduction band of TiO$_2$ from the excited CT state. As the CT complex is strongest with the NO$_2$-Cat, it suggests a complex with a deeper surface state and that delocalization into the conduction band from this state is an uphill process. However, no such differences were observed in Sal derivatives as it forms complex with surface Ti$^{4+}$ states that are higher in energy and near to the conduction band edge or above.

**Figure 4.15** Schematic diagram showing the CT complexation behaviors of Catechol and Salicylate with TiO$_2$ nanoparticles in solution. Also shown in the next schematic are the charge injection and charge delocalization pathways from the excited molecule/TiO$_2$ CT state.

Transient absorption measurements of Cat/TiO$_2$ in solution phase have shown the presence of an excited CT state that recombines with a faster time constant. However, no such excited CT State was observed for Sal/TiO$_2$ where excitation leads to charge separated state followed by multi-exponential charge recombination. The presence of an excited CT state in Cat/TiO$_2$ is attributed to
the fact that Cat forms a strong CT complex with Ti$^{3+}$ defect states while Sal forms a CT complex with Ti$^{4+}$. (Figure 4.14) This CT complex of Cat with Ti$^{3+}$ shows an interesting behavior with respect to donor/acceptor strength of the substituent on catechol. With increasing the strength of acceptor on catechol, the CT complex is stronger and the excited state contribution to the ESA is larger and the charge separation is smaller. MetCat, a donor substituted catechol shows a smaller percentage decay corresponding to the excited CT state and the highest charge separated species. On the other hand, NO$_2$-Cat, the strongest acceptor shows no charge separation initially as the excited CT state dominates its ESA spectral profile. With a decay in the excited CT state, small amount of charge separated species was observed. However, the transient absorption features of Sal/TiO$_2$ and NH$_2$-Sal/TiO$_2$ are similar to one another as the contribution from the excited CT state is smaller in both cases.

Interesting transient absorption features were observed for Cat/TiO$_2$ in solution and thin films. As the defect Ti$^{3+}$ states are smaller in thin films, the ESA of Cat/TiO$_2$ do not show any feature corresponding to the excited CT and the dynamics is dominated by instantaneous formation of charge separated species and interestingly show slow charge recombination. (Figure 4.14) The results show that the Cat/TiO$_2$ thin film systems can be used for photocatalytic applications or solar cells as it leads to efficient charge separated species. However, no differences were observed for Sal/TiO$_2$ in solution and thin films.

4.5. Conclusion

Charge carrier relaxation dynamics in surface CT modified TiO$_2$ nanoparticles was studied with femtosecond time-resolved fluorescence and transient absorption spectroscopy. The major objectives of this study are to probe the influence of donor/acceptor strength on the charge carrier dynamics in catechol and salicylic acid modified TiO$_2$ nanoparticles as well as to understand the
influence of surface morphology on the charge carrier dynamics. Different catechol derivatives were studied namely MetCat, Cat, CN-Cat and NO\textsubscript{2}-Cat, with increasing strength of acceptor on catechol. Optical absorption measurements have shown that all Cat and Sal derivatives modify the surface of TiO\textsubscript{2} via the formation of LMCT complex with surface Ti atoms. Increasing the acceptor strength on catechol lead to stronger CT complex with TiO\textsubscript{2}. Femtosecond time-resolved luminescence measurements have shown ultrafast ICT emission from all small molecule derivatives sensitized TiO\textsubscript{2} and the emission seems to arise from localized excitations. The CT emission decay is a result of both charge delocalization and geminate recombination. Cat and NH\textsubscript{2}-Cat have shown instantaneous ICT emission decay that is assigned to charge delocalization from the excited CT state. However, with an increase in acceptor strength, the emission was slowed down as the delocalization into TiO\textsubscript{2} is an uphill process energetically.

Transient absorption measurements of Cat/TiO\textsubscript{2} have shown the presence of an excited CT state which decays with different time scale than charge recombination. However, no such evidence of excited CT was found for Sal/TiO\textsubscript{2}. This is attributed to the fact that Cat forms stronger CT complex with defect Ti\textsuperscript{3+} states while Sal forms complex with Ti\textsuperscript{4+} states on the surface of TiO\textsubscript{2} nanoparticles. With increased donor strength on Catechol, the charge separation was higher while increasing the acceptor strength on catechol, decreased the efficiency of charge separation but increased the decay contribution from the excited CT state. The results show that donor substituted catechols are suitable candidates to achieve better charge separation. Interesting charge-carrier dynamics was observed for Cat/TiO\textsubscript{2} in thin films. This system in thin films has shown no evidence for excited CT state and the dynamics is dominated by instantaneous charge separation and slow charge recombination. This is rationalized based on the absence of defect Ti\textsuperscript{3+}
states in thin films. The results show that it is possible to achieve greater charge separation with CT modified TiO$_2$ nanoparticles with appropriate choice of substituents and surface morphologies.
4.6. Summary of Chapter 4

- Charge carrier relaxation dynamics in surface CT modified TiO$_2$ nanoparticles is investigated with combined femtosecond time-resolved fluorescence and transient absorption spectroscopy
- The objectives of the study is to probe the influence of donor/acceptor on small molecule on the interfacial charge carrier dynamics and also probe the influence of surface morphology of semiconductor on the charge carrier relaxation dynamics
- Optical absorption measurements have shown that all the small molecules investigated were able to modify the surface of TiO$_2$ nanoparticles by shifting the absorption into visible region
- Femtosecond luminescence was observed from all molecule/TiO$_2$ systems and was assigned to localized ICT emission. The decay was dominated by delocalization of charges into the conduction band of TiO$_2$
- Increasing the acceptor strength on catechol decreased the rate of delocalization as the CT complex is formed with deeper surface states
- Transient absorption measurements have shown the presence of excited CT state for Cat/TiO$_2$ in solution, while no such state is observed for Sal/TiO$_2$. This is attributed to the fact that Cat forms a CT complex with defect Ti$^{3+}$ states while Sal forms a complex with Ti$^{4+}$
- Increasing the acceptor strength on catechol increased the contribution of the excited CT state and decreased charge separation
- Charge separation was highest for Cat/TiO$_2$ in thin film and no evidence of excited CT was observed as thin film has smaller density of defect Ti$^{3+}$ states
4.7. References


CHAPTER 5

ULTRAFAST INTERFACIAL CHARGE-TRANSFER DYNAMICS IN ANTHRACENE AND PYRENE CATECHOL FUNCTIONALIZED TiO₂ NANOPARTICLES

5.1. Introduction

In the previous chapter, the charge-carrier dynamics of surface charge-transfer (CT) modified TiO₂ nanoparticles was discussed. The results have shown that the localized charge-transfer states created by surface modifiers dominate the charge carrier dynamics where the strength of the donor/acceptor on the modified surface modified influence the charge separation and recombination dynamics. However, the surface modifiers have limited absorption in the visible region. Attaching the dye molecules to the surface modifiers would enhance the visible light absorption. However, the dynamics of charge carriers with this arrangement would be affected both by charge-transfer states of surface modifiers and the dye molecules that are attached to it. It would be interesting to know which chromophoric structure would dominate the charge relaxation dynamics. A schematic of the dye-surface modified semiconductor under investigation is shown in Figure 5.1. The charge-carrier dynamics in these geometries are quite important for addressing the interfacial charge-transfer concerns that are important for dye solar cells and catalysis.
Figure 5.1 Schematic diagram of the dye-surface CT modified TiO$_2$ nanoparticles.

Charge transfer processes in semiconductor nanomaterials and molecule-semiconductor interfaces has been in the forefront of research for last three decades. This is because of their applications in photography$^1$, nano-scale devices$^2$, photocatalysis$^3$, and solar energy conversion$^4$. Many molecule/semiconductor nanoparticles systems have been studied, some of them include TiO$_2$ and ZnO bound to organic adsorbate molecules. Sensitizer molecules adsorbed on surface of the semiconductor nanoparticles absorb the visible light and aid in charge separation. The dynamics of charge-transfer at a sensitizer-semiconductor interface has been investigated by several researchers for last decades as it presents a heterogeneous electron transfer problem as well as finding applications in dye-sensitized solar cells (DSC). In typical DSCs, the excited sensitizer molecules inject electrons into the conduction band of TiO$_2$ nanoparticles where charges would be separated and the electrons are collected at the conducting electrode giving rise to electric voltage output. Several organic dye molecules have been studied that include merocyanine$^{5,6}$, hemicyanin$^{7-9}$, porphyrin$^{9-14}$, phthalocyanine$^{15-16}$, indoline$^{17,18}$, squaraine$^{19-21}$ and coumarins dyes$^{22-25}$. With these organic dye molecules, solar cell efficiencies of over 9% have been achieved$^{5-25}$. 

119
The most common anchoring groups used for binding the sensitizers to TiO$_2$ surface are carboxylate, phosphonates, sulfonic acids, silanes, amides and esters (Type-1). These anchoring groups are innocent and do not create additional states with semiconductors. On the other hand, ene-diol molecules such as catechol and salicylic acids (discussed in Chapter 4) present an interesting proposition wherein these small molecules not only can act as stable anchoring groups but also provide additional charge-transfer states in the semiconductor nanoparticles. This type of binder is often termed as Type-2. An enormous amount research has focused on Type-1 binding interactions but similar work on Type-2 has been limited. In an earlier work, pyrogallol red and bromo pyrogallol red were used to sensitize TiO$_2$ and interesting ultrafast charge injection and charge recombination were observed. Also, some work has also focused on porphyrin and Ru-polypyridyl complexes with catechol (Type-2) as anchoring groups. However, the detailed understanding of the role of surface CT modifier and the chromophore is not available. It will also be interesting to see how the solution versus thin film phases can influence the dynamics of charge carriers. To understand these parameters, dynamics of charge-carriers was studied on two organic dye molecules (anthracene and pyrene) with catechol as an anchoring group. Catechol groups provide the Type-2 interaction while the organic molecules work as sensitizers. Anth-Cat and Pyr-Cat (molecular structures are shown in Figure 5.2) were synthesized and the dynamics of charge carriers was probed with femtosecond fluorescence upconversion and transient absorption both in solution and thin film phases.
5.2. Materials

Titania paste was obtained from Solaronics inc., and Indium Tin Oxide (ITO) covered glass slides were purchased from Nanocs and were used as such. Titanium (IV) tetraisopropoxide was obtained from Aldrich and was used as such. Nanopure water has been utilized to carry out all the measurements unless stated otherwise. The materials used for the synthetical experimentation were catechol, anthracene-2-amine, pyren-1-amine, 3,4-dihydroxybenzaldehyde, ethanol, methanol and isopropanol (2-propanol) were obtained from Sigma-Aldrich and were used as received.

5.2.1. Synthesis of TiO$_2$ Nanoparticles

TiO$_2$ nanoparticles were synthesized by the controlled hydrolysis of titanium (IV) tetraisopropoxide.$^{46,47}$ Briefly, 10 mL of Ti[OCH(CH$_3$)$_2$]$_4$ was dissolved in 90 mL of isopropyl alcohol and was added drop wise at a rate of 1 mL min$^{-1}$ to 900 mL of nanopure water (pH 1.5-adjusted with HNO$_3$) with continuous stirring. The stirring was continued for a period of 12 h. A transparent colloid was formed which was then concentrated at 308-313 K with a rotary evaporator. The resulting powder was then dried under nitrogen to yield a white powder.

**Figure 5.2** Molecular structures of the investigated chromophores.
5.2.2. Fabrication of TiO$_2$ Films

A well established procedure for the assembly TiO$_2$ films was used.$^{48}$ ITO glass slides were cut into squares using a diamond cutter that were then washed and air dried. The doctor blading method was used to make transparent TiO$_2$ films. The films were allowed to dry for 5 minutes after which they were placed in an oven for 45 minutes at 723 K to bake. They were then taken out and allowed to cool down to room temperatures before being immersed in the selected sensitizer solutions for 30 minutes. They were then taken out and washed with methanol to remove any un-adsorbed dye.

5.2.3. Synthesis of (E)-4-((anthracen-2-ylimino) methyl) benzene-1,2-diol (AnthCat)

The synthetic scheme for AnthCat is provided on Figure 5.3. (Collaboration with Prof. Ekkehard Sinn) In a 25 mL flask, anthracene-2-amine (0.30g, 1mmol) and 3, 4-dihydroxybenzaldehyde (0.21 g, 1 mmol) were suspended in 20 mL ethanol. The mixture was refluxed for 12 hr with stirring, during which time an orange precipitate formed. The precipitate was separated by filtration and washed with 3 x 10 mL ethanol. After drying, a bright orange solid in 80% yield was obtained. The product was characterized by $^1$H NMR and mass spectrometry.
5.2.4. Synthesis of (E)-4-((pyren-1-ylimino) methyl) benzene-1, 2-diol (PyrCat)

The synthetic scheme for PyrCat is provided on Figure 5.3. (Collaboration with Prof. Ekkehard Sinn) In a 25 mL flask, pyren-1-amine (0.20g, 1mmol) and 3, 4-dihydroxybenzaldehyde (0.13g, 1mmol) all were suspended in 20mL ethanol. The mixture was refluxed for 12 hr with stirring, during which time a yellow precipitate formed. The precipitate was separated by filtration and washed with 3 x 10 mL of ethanol. After drying, yellow solid in 78% yield was obtained. It was characterized by $^1$H NMR and mass spectrometry.

Figure 5.3 Mechanistic scheme depicting the synthesis of AnthCat
Figure 5.4 Mechanistic scheme depicting the synthesis of PyrCat

5.3 Methods

Optical absorption measurements were carried out using a Shimadzu UV 2101 PC absorption spectrometer. Benesi-Hildebrand analysis was used to determine the association constants which will be discussed in the main text. Time resolved fluorescence and fluorescence anisotropy of molecule/TiO$_2$ nanoparticles were studied using the femtosecond fluorescence upconversion with a procedure described elsewhere.$^{49}$ The upconversion system used in our experiments was obtained from a CDP system with a design that is similar to what has been published elsewhere.$^{49}$ Briefly, the system used frequency doubled (400 nm) light from a mode-locked broadband Ti-sapphire laser (Spectra Physics, Tsunami, 710-920 nm). For this system, the sample is continuously rotated with a rotating cell, which is 1 mm thick, to avoid the degradation of the sample. The horizontally polarized fluorescence which was emitted from the sample was
upconverted in a nonlinear crystal of β-bariumborate using a pump beam at 800 nm, which first passed through a variable delay line. Instrument response function (IRF) was measured using Raman scattering from water. Fitting the Gaussian peak from the Raman scattering yielded a sigma value of \( \sim 130 \) fs which gave a full width half maximum of \( \sim 250 \) fs.

The spectral resolution was attained by using a double monochromator and photomultiplier tube. The excitation average power varied during experiments but was mostly in the range of \( 21 \pm 0.5 \) mW. The time-resolved fluorescence anisotropy \( (r(t)) \) measurements were carried out with parallel and perpendicular excitations in which the polarization was changed with a Berek compensator. Fluorescence anisotropy was calculated from the traces obtained from the parallel and perpendicular excitation using a method \(^{49-51}\) which is based on the ratio of difference between parallel and perpendicular polarized emissions over the magic-angle fluorescence.

Femtosecond transient absorption investigations were carried out using an ultrafast pump-probe spectrometer which a detection response for the visible electromagnetic region located at Argonne National Laboratory and the experimental description is describe in chapter of this dissertation and is explain in detail elsewhere.\(^ {52}\) To explain in brief detail, 1 mJ, 100 fs pulses at 800 nm with a repetition rate of 1 KHz were retrieved from a Nd:YLF (Empower) pumped Ti:sapphire regenerative amplifier (Spitfire, Spectra-Physics) with the input from a Millennia pumped Ti: sapphire oscillator (Spectraphysics, Tsunami). The output of laser beam was split to generate pump and probe beam pulses with a beam splitter (85% and 15%). The pump beam was produced by an optical parametric amplifier. The pump beam used is described in previously, i.e., 420 nm, was obtained from the fourth harmonic of the idler beam. The probe beam was delayed with a computer-controlled motion controller and then focused into a 2 mm sapphire plate to generate a white light continuum. The white light was then overlapped with the pump beam in a 2
mm quartz cuvette containing the sample, and the change in absorbance for the signal was collected by a CCD detector (Ocean Optics). Data acquisition was controlled by the software from Ultrafast systems Inc. The typical power of the probe beam was around 10 µJ/cm² while the pump beam was around 1000 µJ/cm². The magic angle polarization was maintained between the pump and probe using a wave plate. The pulse duration was obtained from the non-resonant fitting of the solvent response, which was around 130 fs. The samples were stirred by a rotating magnetic stirrer and little degradation of the sample was observed during the experiments. Blank experiments were carried out with bare TiO₂ nanoparticles, and water and minimal signal was observed, as they do not possess absorption at the excitation wavelength of 420 nm.

5.4. Results and Discussion

5.4.1. Optical Absorption Measurements

Optical absorption spectra of AnthCat and PyrCat molecules in methanol and on the surface of TiO₂ in solution and on thin films are shown in corresponding graphs of Figure 5.5. The spectra were normalized to the maximum absorbance of the lower energy absorption band and it can be observed that the optical density of both systems is influenced with the adsorption onto the surface of TiO₂ nanoparticles both in solution and on thin films. It can be observed in Figure 5.5A that the absorption spectrum of AnthCat became broader and shifted to the longer wavelengths when bound to the TiO₂ nanoparticles indicating a strong ground state electronic interaction with TiO₂ surface. Similar red shift and broadening was observed for PyrCat bound to the TiO₂ surface. (Figure 5.5B) Also, the fluorescence of AnthCat and PyrCat were quenched significantly when bound to TiO₂ nanoparticle surface suggesting efficient charge injection from the excited state of dye molecule to TiO₂. (Figure 5.5 C and 5.5 D) To further probe the dynamics of charge-injection, femtosecond time-resolved measurements were carried out.
Figure 5.5 Normalized optical absorption of AnthCat (A) and PyrCat (B) in methanol and on the surface of TiO2 nanoparticles in solution and on thin films. Normalized fluorescence spectra of AnthCat (C) and PyrCat (D) in solution and on the surface of TiO2 nanoparticles. Both dyes display quenched fluorescence when adsorbed to the surface of the TiO2 nanoparticles.

5.4.2. Association Constants of Molecule/TiO2 Nanoparticles: Benesi-Hildebrand Analysis

The association constants of the AnthCat/TiO2 and PyrCat/TiO2 complexes were determined from Benesi-Hildebrand plots.\textsuperscript{53} Benesi-Hildebrand analysis works with the assumption that there is a 1:1 complexation between the molecules to surface Ti atoms. Further explanation of equations used can be seen in previous chapter of the presented dissertation. The Benesi-Hildebrand plots for anthracene catechol and pyrene catechol are displayed in parts A and
B of Figure 5.6, respectively. A ratio of intercept to slope provides the required association constant values which are provided in Table 5.1.

![Absorption spectra](image)

**Figure 5.6** Absorption spectra of the investigated molecule/TiO$_2$ systems with an increase in TiO$_2$ concentration for (A) AnthCat/TiO$_2$ and (B) PyrCat/TiO$_2$

**Table 5.1** The association constants for different Anth-Cat and Pyr-Cat TiO$_2$ nanoparticles

<table>
<thead>
<tr>
<th>[Dye/TiO$_2$] Molecule</th>
<th>Association Constant $K_a$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AnthCat/TiO$_2$</td>
<td>$4.4 \pm 0.7 \times 10^3$</td>
</tr>
<tr>
<td>PyrCat/TiO$_2$</td>
<td>$1.0 \pm 0.6 \times 10^3$</td>
</tr>
</tbody>
</table>

5.4.3. Femtosecond Fluorescence Upconversion Measurements

To monitor the dynamics of charge injection, femtosecond fluorescence measurements were carried out. Steady-state fluorescence measurements have shown quenched luminescence for the dyes on the surface of TiO$_2$ nanoparticles in solution. Femtosecond luminescence dynamics measurements can reveal the dynamics of charge injection in these systems. Before proceeding onto the fluorescence measurements of the sensitzers on TiO$_2$ surface, it is important to understand the free dye molecules in solution. AnthCat and PyrCat do not readily dissolve in water, so the
free dye fluorescence measurements were carried out in ethanol. Shown in Figure 5.7A is the fluorescence kinetic decay trace of AnthCat in ethanol at an emission wavelength of 500 nm after excitation at 400 nm. It can be observed that the fluorescence of AnthCat decays very fast and the decay traces ($F(t)$) were fit using a three exponential function:

$$F(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} + a_3 e^{-t/\tau_3} \quad \text{Equation 5.1}$$

Where $a_1$, $a_2$ and $a_3$ are amplitudes and $\tau_1$, $\tau_2$ and $\tau_3$ are the corresponding lifetimes. Average lifetimes ($\tau_{av}$) were determined using the following equation:

$$\tau_{av} = \frac{\sum a_i \tau_i}{\sum a_i} \quad \text{Equation 5.2}$$

From the analysis, time constants of 220 fs (73.7%), 1.2 ps (23.1%) and $> 100$ ps (3.2%) were obtained. Ultrafast fluorescence time constants for AnthCat were attributed to cis-trans isomerization or charge-transfer from the amine donor to the anthracene core.

**Figure 5.7** Fluorescence decay traces of (A) AnthCat in methanol at 500 nm and (B) PyrCat in methanol at 480 nm. Also, shown in the insets are corresponding anisotropy decay traces.
Similarly, fluorescence upconversion measurements were carried out for PyrCat in methanol after excitation 400 nm and shown in Figure 5.7B. It can be observed that the fluorescence decay of PyrCat also decays very fast and the fast decay was complete in 1 ps with a residual slower component living for longer time. The decay was fitted with time constants of 0.11 ps (91.7%), 0.41 (7.8%) ps and > 1000 ps (0.5%). More than 99% decayed fast suggesting efficient electron transfer from amine moiety to pyrene core. It is interesting to see if there is any electron injection possible from these dye molecules as the excited state decays so fast. Steady-state fluorescence measurements show efficient fluorescence quenching in the presence of TiO$_2$ nanoparticles, indicating charge injection from the dyes to TiO$_2$. To probe the dynamics of charge injection, fluorescence upconversion measurements are carried out on the dyes bound to TiO$_2$ nanoparticle surface.

Ultrafast ICT emission was observed from the AnthCat/TiO$_2$ complex and the luminescence decay kinetics of AnthCat/TiO$_2$ were monitored after excitation at 400 nm at the different emission wavelengths of 500, 520, 550 and 580 nm and shown in Figure 5.8. The instrument response limited decay dominates the emission decay for the AnthCat/TiO$_2$ system in solution. With an increasing wavelength, the emission decay is always fast indicating ultrafast charge injection from the dye to TiO$_2$. The decay traces were fitted with 120 fs (96%) and 1.2 ps (4%). All the fluorescence decay traces were wavelength independent and they are attributed to charge delocalization into the conduction band of TiO$_2$ after the excitation populates a localized charge-transfer excitonic state. This phenomenon is similar to what was observed small molecule such as catechol modified TiO$_2$ nanoparticles. Overall, the AnthCat on the surface of TiO$_2$ in solution shows ultrafast charge injection. Further transient absorption measurements would help provide needed information about the charge transfer dynamics.
Similar to AnthCat/TiO$_2$, fluorescence upconversion measurements were carried out on PyrCat/TiO$_2$ after the excitation at 400 nm. The fluorescence decay traces were monitored at 520, 550, and 580 nm respectively and are shown in Figure 5.9. The decay traces again were fitted with time constants of 100 fs (95%) and 1.2 ps (5%) and these time constants can be attributed to charge delocalization from the localized CT excitonic state. It was interesting to observe ultrafast charge transfer from PyrCat to TiO$_2$ even though its excited state decays fast. This can be ascribed to strong electronic coupling of chromophore with TiO$_2$. 

Figure 5.8 Femtosecond luminescence decay traces AnthCat/TiO$_2$ at different wavelengths.
Figure 5.9 Femtosecond luminescence decay traces for PyrCat/TiO$_2$ nanoparticles in solution at different emission wavelengths.

5.4.4. Femtosecond Transient Absorption Measurements

Fluorescence upconversion measurements have shown ultrafast charge injection from the dye molecules to TiO$_2$ even though free dye molecule’s fluorescence decays fast. To further understand the dynamics of charge carriers in these dye/TiO$_2$ interfaces, femtosecond transient absorption measurements were carried out. The transient absorption measurements can monitor the excited charge transfer states as well as the catio radical or electron in the conduction band, and the electron injection and charge recombination dynamics. Before describing the transient characteristics of chromophore/TiO$_2$ composites, it is important to understand the excited state dynamics of free dye molecules in solution.

Shown in Figure 10A are the excited state absorption (ESA) features at short time delays from 50 fs to 1.2 ps for AnthCat dissolved in methanol after excitation at 420 nm. At a time delay of 100 fs, the ESA is dominated by positive feature at 490 nm and another at 650 nm. With increase in time delay to 1.2 ps, these features decay to give rise to negative signal at 460 nm and 550 nm along with a shift in ESA to 500 nm. These features can be assigned to relaxation from Franck-Condon state to another state, probably a charge-transfer state. The negative features are assigned to stimulated emission from the dye molecules. This state decays with time from 1.5 ps to 700 ps (Figure 5.10 B) with a bleach recovery as well as a shift in positive absorbance to 490 nm. This suggests that the charge-transfer state relaxes pretty quickly to give rise to long-lived state with a lifetime of > 1 ns. All the kinetics at different wavelengths was fitted using global fit analysis and corresponding species associated spectra obtained from the analysis is presented in Figure 5.10 C. It is quite evident from the Figure that the decay traces fit well with time constants of 220 fs, 1.2
ps whose ESA match with that of an initial ESA followed by a decay component of 6.1 ps to give rise to long-lived state. The first two components obtained from the analysis match well with that of fluorescence upconversion measurements and were assigned to charge transfer from amine donor to anthracene core that recombines to give rise to long-lived singlet state.

![Graphs showing ESA of AnthCat in methanol at different time delays](image)

Figure 5.10 (A) ESA of AnthCat in methanol at time delays from 50 fs to 1.2 ps and (B) from 1.5 ps to 700 ps. (C) Species associated spectra obtained from global fit analysis

On the other hand, the transient absorption features of PyrCat in methanol are quite different. Shown in Figure 5.11A are the ESA at different time delays from 100 fs to 2.2 ps and
by that time most of the transients had decayed suggesting ultrafast excited state relaxation. The decay traces were fit with time constants of 130 fs and 450 fs and > 2 ps (Figure 5.11B). The positive absorption features are assigned to fast excited state relaxation due to charge transfer from amine core to pyrene with time constants of 130 fs and 450 fs followed by long-lived excited state whose absorption features are not observable in the monitored time window. The time constants obtained from transient absorption matched closely to that of fluorescence upconversion. It is interesting to note ultrafast excited state decay for free dyes and how these dye molecules can inject their charges to the surface of TiO$_2$ remains to be seen.

Figure 5.11 (A) Excited state absorption of PyrCat in solution with (200 fs to 800 ps) time delays (B) Charge recombination trace monitored at 640 nm of the PyrCat free dye solution

Transient absorption measurements were carried out for the dyes adsorbed onto TiO$_2$ nanoparticles in solution and on thin films to probe the nature of the semiconductor on interfacial charge carrier dynamics. Shown in Figure 5.11A are ESA spectra at different time delays from 50 fs to 1 ns for AnthCat/TiO$_2$ nanoparticles in solution after excitation at 420 nm. As observed from the transient absorption features of free dye, the ESA decays fast for free dye. However, the ESA
at 100 fs for AnthCat/TiO$_2$ has shown entirely different features with an ESA maximum at 630 nm and a bleach around 460 nm. The bleach feature matches well with that of surface CT modified TiO$_2$. The positive ESA feature is assigned to the localized cation radical of AnthCat. However, the ESA at 630 nm as well as bleach recovers with multi-exponential relaxation time constants. Species associated spectra obtained from global fit analysis is shown in Figure 5.11B. Global fit analysis has shown ultrafast charge injection (<100 fs) matched well with femtosecond fluorescence measurements, followed by multi-exponential charge recombination with time constants of 850 fs, 7.5 ps, 185 ps and > 1 ns. The results show that there is still significant charge separation, indicating these dye molecules can be used in the context of solar cells.

Figure 5.12 (A) ESA at different time delays for AnthCat/TiO$_2$ in solution after excitation at 420 nm. (B) Species associated spectra obtained from global fit analysis

Time-resolved transient absorption measurements were also carried out for AnthCat/TiO$_2$ thin films after excitation at 420 nm. Shown in Figure 5.12A are the ESA at different time delays for AnthCat/TiO$_2$ thin film. The ESA of AnthCat/TiO$_2$ thin film has shown similar
features as that of AnthCat/TiO$_2$ in solution with ESA maximum around 610 nm and another maximum at 520 nm. With increase in time delay, this ESA decays to give rise to broad ESA at 630 nm and 510 nm. When compared to solution phase measurements, the bleach is absent in thin films. This can be attributed to differences in the extinction coefficients of ESA in films. Species associated spectra obtained from global fit analysis has shown same 850 fs matched well with that of AnthCat/TiO$_2$ in solution as well as that of thin films. This is attributed to the charge-transfer exciton recombination from the dye to TiO$_2$. However, significantly greater charge separation is observed for AnthCat/TiO$_2$ with much slower recombination time constants, suggesting that this dye molecule can be a potential solar cell sensitizer.

![Figure 5.13](image.png)

**Figure 5.13** (A) ESA at different time delays for AnthCat/TiO$_2$ thinfilm after excitation at 420 nm. (B) Species associated spectra obtained from global fit analysis

Kinetic decay traces for AnthCat/MeOH, AnthCat/TiO$_2$ in solution and AnthCat/TiO$_2$ thin film were compared at their ESA maximum and are shown in Figure 5.13. It is quite evident from the figure that even though the ESA of free AnthCat has decayed very fast, it was able to inject
electrons efficiently into the conduction band of TiO$_2$ both in solution and thin film phases. The results show that the strong interfacial electronic coupling of surface modifier made ultrafast charge injection possible. Also, it is quite interesting to see that the charge separation is more efficient in thin film phases as the relative number of trap states are far lower in thin film phases.

![Figure 5.14](image)

Figure 5.14 Kinetic decay trace comparison for AnthCatA/MeOH, AnthCat/TiO$_2$ in solution and on thin film and their ESA maxima

Overall, one can observe that charge recombination dynamics is slower on the surface of thin films when compared to the systems in solution form. Table 5.2 summarizes the charge injection and charge recombination time constants as determined from the transient absorption measurements. The results show significant charge separation for AnthCat sensitized TiO$_2$ nanoparticles both in solution and thin film phases suggesting that strongly coupled dye molecules can still be used for solar cell applications.
Table 5.2 Summary of ESA lifetimes for AnthCat in various media

<table>
<thead>
<tr>
<th></th>
<th>AnthCat/MeOH</th>
<th>AnthCat/TiO(_2) in solution</th>
<th>AnthCat/TiO(_2) on thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESA lifetimes</td>
<td>220 fs, 1.2 ps, 6.1 ps and &gt; 1 ns</td>
<td>100 fs ((\tau_{\text{inj}})) 850 fs, 7.5 ps, 185 ps and &gt; 1 ns ((\tau_{\text{CR}}))</td>
<td>100 fs ((\tau_{\text{inj}})) 850 fs, 85 ps and &gt; 1 ns ((\tau_{\text{CR}}))</td>
</tr>
</tbody>
</table>

Similar time-resolved absorption measurements were carried out on PyrCat/TiO\(_2\) in solution and on thin film phases after exciting at 420 nm. Transient absorption data of PyrCat in MeOH has shown ultrafast excited state decay. It will be interesting to see if the dye can inject electrons into TiO\(_2\) or not. Shown in Figure 5.14A are the ESA at different time delays for PyrCat/TiO\(_2\) from 100 fs to 1 ns. The ESA at 100 fs has shown a positive maximum at 645 nm with bleach maximum at 450 nm. The bleach is ascribed to Catechol/TiO\(_2\) charge-transfer complexation and the ESA maximum at 645 nm is attributed to the cation radical of PyrCat. As the time delay is increased, bleach is recovered along with the decay of cation radical of PyrCat and is assigned to charge recombination. So, even with PyrCat, ultrafast charge injection to TiO\(_2\) is observed with multi-exponential charge recombination. Species associated spectra obtained from global fit analysis is shown in Figure 5.14 B. Species associated spectra of all the time constants are pretty much similar except for that of the long time component. First three time constants are 800 fs, 10 ps and 185 ps arise from geminate recombination of the electron in the conduction band and the cation radical of PyrCat. The long time recombination arises from the charge delocalized into TiO\(_2\) and the cation radical localized on Pyrene. The results show that there is efficient charge separation with this system, with as much as 30% of ESA not decaying till 1 ns.
Even though the singlet state lifetime is very fast for the PyrCat, it shows efficient charge injection into TiO$_2$ and multi-exponential charge recombination.

**Figure 5.15** (A) Excited state absorption of PyrCat/TiO$_2$ in solution at different time delays from 100 fs to 1 ns and (B) Species associated spectrum obtained from global fit analysis.

Transient absorption measurements were also carried out for PyrCat/TiO$_2$ thin film phases. Figure 5.15A shows the ESA at different time delays for PyrCat/TiO$_2$ from 100 fs to 900 ps. The ESA at 100 fs shows a positive feature with a maximum at 615 nm. This ESA that can be assigned to cation radical of the dye is different from that of PyrCat/TiO$_2$ in solution. This difference can be attributed to the solvent environment around the dye molecule that can shift the ESA of the cation radical. A similar effect was observed for AnthCat, as well as for several other dye molecules such as Alizarin and quinizarin on different TiO$_2$ phases. Also, there is no clear bleach in the ESA spectrum of PyrCat/TiO$_2$ thin film, a clear difference from what was observed in solution. This discrepancy arises from the fact that the CT complexation of catechol on thin film is very weak and no bleach is observed in such systems. So, it is possible to realize no bleach from
Cat/TiO₂ complex in thin film phases. However, as the time delay is increased the ESA decays, but more than 50% of ESA did not decay until 900 ps indicating efficient charge separation. Species associated spectra of PyrCat/TiO₂ was also determined from global fit analysis and shown in Figure 5.15B. It gave only two time constants of 3.9 ps and > 1 ns. Fast charge recombination is assigned to geminate charge recombination from the electron in the conduction band of TiO₂ and the cation radical of PyrCat. But, PyrCat/TiO₂ thin film shows slow charge recombination emphasizing its value in dye solar cells.

![Figure 5.15A](image1.png)

**Figure 5.15** (A) ESA of PyrCat/TiO₂ thin films from 100 fs to 900 ps and (B) species associated spectrum obtained from global fit analysis

Kinetics decay traces at respective ESA for PyrCat in MeOH and on TiO₂ in solution and thin film at their respective ESA maxima are shown in Figure 5.16. It is evident from Figure that PyrCat decays in ultrafast time scales. However, PyrCat/TiO₂ thin film shows ultrafast charge injection followed by mult-exponential recombination with some amount of transients not decaying until 1 ns. However for PyrCat/TiO₂ thin film phase, ESA decays only with 3.9 ps time

![Figure 5.16](image2.png)
component and more than 50% charge not recovered until 900 ps. The results show that PyrCat can be a good sensitizer for dye based solar cells. Obtained ESA lifetimes for PyrCat in different media are summarized in Table 5.3.

**Figure 5.17** Kinetic decay trace comparison for PyrCat/MeOH. PyrCat/TiO$_2$ in solution and on thin film

**Table 5.3** ESA lifetimes of PyrCat in various media

<table>
<thead>
<tr>
<th>lifetimes</th>
<th>PyrCat (MeOH)</th>
<th>PyrCat/TiO$_2$ in solution</th>
<th>PyrCat/TiO$_2$ on thinfilm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>120 fs and 2.2 ps</td>
<td>100 fs ($\tau_{\text{inj}}$)</td>
<td>100 fs ($\tau_{\text{inj}}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800 fs, 10 ps, 185 ps and &gt; 1ns ($\tau_{\text{CR}}$)</td>
<td>3.9 ps and &gt; 1ns ($\tau_{\text{CR}}$)</td>
</tr>
</tbody>
</table>

**5.5. Mechanism of Charge Carrier Pathways in DyeCat/TiO$_2$ Systems**

Overall, from the measurements of charge-transfer dynamics in dye-surface CT modified TiO$_2$ nanoparticles, three important things were observed. Firstly, the electronic coupling is strong with catechol binding to TiO$_2$ and the charge injection from the dyes to TiO$_2$ surface is instrument limited. Secondly, the charge injection from the excited state of dye and charge delocalization from
the localized CT state was observed. Finally, the charge recombination is multi-exponential and
significant charge separation is observed in thin film phases compared to solution phase indicating
the use of these dye/semiconductor architectures for dye solar cell applications. The mechanism
of charge-carrier dynamics in these dye/CT-modified TiO₂ architectures is depicted in Scheme 5.1.
Femtosecond transient absorption and fluorescence upconversion measurements have shown
ultrafast charge injection because of strong electronic coupling offered by charge-transfer forming
anchoring group. However, evidence of charge delocalization is still observed in solution
indicating the involvement of localized CT states due to Type II injection. However, direct charge
injection into conduction band of TiO₂ was observed similar to that of Type I injection. The charge
recombination is multi-exponential with electrons trapped at different trap states. Since the density
of trap states is smaller in thin films, the charge recombination is slower and larger charge
separation was observed.

Figure 5.18 Mechanistic scheme depicting the charge-carrier dynamics in dye-CT modified TiO₂
nanoparticles.
5.6. Conclusion

The main objective of this study is to understand the influence of surface CT modification on charge-carrier dynamics of sensitizer/semiconductor nanoparticle systems. To accomplish the objective, chromophores with CT forming anchoring groups (AnthCat and PyrCat) were synthesized via Schiff-base condensation. The excited state dynamics of AnthCat and PyrCat were dominated by ultrafast decay components arising out of charge-transfer from amine moieties to the core of dye molecules. However, when the dyes are attached to TiO$_2$ nanoparticles, efficient charge injection to the surface of TiO$_2$ is observed. Femtosecond fluorescence upconversion and transient absorption measurements have shown evidence for ultrafast charge injection with contribution from both Type I and Type II injection pathways. However, components for charge delocalization into TiO$_2$ were observed as well. The charge delocalization components for both dyes are more evident in solution than on thin films. The charge recombination dynamics was found to be multi-exponential with significant component of greater than 1 ns. The study shows that dye/CT-semiconductor nanoparticles also can lead to efficient charge separation. Interestingly, long-lived charge separation is higher with thin film samples compared to solution phase. The long-lived charge separation in thin films is attributed to lower density of trap states in thin films when compared to nanoparticles in solution. Overall, the results show that CT forming anchoring groups can be used for solar cell applications and they also give long-lived charge separation similar to that of carboxylate anchoring groups.
5.7. Summary of Chapter 5

- Ultrafast charge carrier dynamics in chromophores with catechol as an anchoring group to TiO$_2$ nanoparticles was investigated to understand the role of surface CT excitons on the interfacial charge transfer dynamics
- Anthracene and Pyrene dye molecules with catechol anchoring group were synthesized via Schiff-base condensation
- Dye molecules in solution have shown ultrafast excited state relaxation due to electron transfer from amine to the core of the dye
- Even though the lifetimes are faster for free dyes, they have shown evidence for ultrafast charge injection with time constants of less than 100 fs. The charge injection is a combination of both Type I and Type II injection.
- The charge recombination was found to be multi-exponential with significant contribution from long-lived charge separated states.
- Charge separation is higher with thin film samples when compared to solution phase and is assigned to lower density of trap states in thin films
- The results have shown that dyes with catechol as anchoring group can be used for solar cell applications even though catechol group can alter the semiconductor surface with CT states.
5.8. References


CHAPTER 6

ZNO/GRAPHENE OXIDE NANOCOMPOSITES AS DISSOLVED OXYGEN SENSORS

6.1. Introduction

Previous chapters of the dissertation have focused on the charge carrier dynamics of semiconductor nanostructures that include the dynamics in quantumsized ZnO nanoparticles (Chapter 3), reactive small molecule surface-modified TiO$_2$ nanoparticles (Chapter 4) and reactive dye molecule surface-functionalized TiO$_2$ nanoparticles (Chapter 5). This chapter of dissertation deals with an application of the optical properties of ZnO nanomaterials in the development of a turn-on luminescent dissolved oxygen sensor.

The demand for intelligent sensor and detection devices is increasing because of their need in a vast array of technological applications. Most importantly, their use is catered for safeguarding environmental and human resources against dangerous agents whether natural or manmade.\textsuperscript{1-5} An ideal sensor should be cost-effective, quickly responsive and capable of detecting low level concentrations of responsive components such as toxic pollutant and biological particulates.\textsuperscript{1-5} Environmental monitoring applications incorporate the detection of biological components in various systems, the quality of air for monitoring harmful volatile constituents, soil particulates that can saturate through many geographical terrains, and more importantly water quality.\textsuperscript{3}

There are several types of sensors such as electrochemical, mass sensitive (acoustic wave sensing), heat sensing, magnetic and optical sensing.\textsuperscript{5} Optical sensors, recently termed optodes or optrodes rely on the principles of absorption and emission.\textsuperscript{3-11} Optical sensors are routinely used
to monitor several analytes such as glucose, different type of enzymes, pH in a cell, and dissolved oxygen. One important analyte that has applications in several areas is that of dissolved oxygen (DO). The detection of DO found applications in water quality management, blood oxygen level monitoring, aquatics, pharmaceuticals, aeronautics and oil spills. Currently, there are several methods that are used to detect DO that include Winkler detection methods, Clark electrodes, and luminescent based optical sensors. The basis of the Winkler titration is the use of oxidation of bivalent manganese from the oxygen dissolved in water that produces a tetravalent compound. This method has limitations due to sample turbidity along with the cost for materials. Polargraphic methods or Clark-type electrodes operate on the principle in which oxygen contained in a sample comes in contact with a gas permeable layer (or membrane), current flow from the cathode to the electrode is altered thereby signaling the DO. Some common negative factors include the membrane transport properties, electrolyte properties, membrane layer thickness, and current flow.

Dynamic luminescence quenching methods with the use of optical detectors have been deemed useful for DO sensing since the late 1930’s. The most common principles used in optical detectors are based on dynamic collision fluorescence quenching, which incorporates the fluorescence quenching of oxygen as a triplet molecule efficiently quenching the fluorescence of specific luminophores. Current optical methods have done a remarkable job of detecting DO, but suffer from the sensitivity issues. Thus, there is a need for low cost real-time DO sensors with improved sensitivity, spectral range, and detector response time. Current optical detection methods have complications in detecting small changes of DO as they are turn-off. On the other hand, turn-on luminescent sensors can solve the limitations of existing optical techniques for DO sensing. The development of a turn-on luminescence based DO sensor is the main motivation of the study.
To achieve the objective, we propose to use ZnO nanoparticles to sense DO. The precedence is that the trap-state luminescence of ZnO nanoparticles arise out of the electrons trapped at oxygen vacancies and gives luminescence only when oxygen is present and gives reduced luminescence when oxygen is not present. Thus, we propose to use this quality of ZnO nanoparticles to develop turn-on luminescent DO sensors. Our overall goal for this project is to develop a novel turn-on luminescent sensor to detect oxygen in complex environments. The hypothesis is that ZnO nanoparticles can function as turn-on luminescent sensor for DO. In addition, measurements were carried out to improve the sensitivity of ZnO nanoparticles to detect DO by incorporating GO nanocomposites as a platform for enhancement. Femtosecond luminescence measurements were also carried out to understand the mechanism underlying the sensing abilities of the ZnO/GO nanocomposites.

6.2. Experimental

6.2.1. Materials and Methods

Zinc acetate, lithium hydroxide monohydrate were obtained from VWR and were used as such. Graphire powder was obtained from Nanocs inc and was used as such. Potassium nitrate, potassium permanganate, sulfuric acid, hydrogen peroxide were obtained from Sigma and were used as such. Optical absorption measurements were carried out in a Shimadzu UV-2102PC spectrophotometer. An Edinburgh F900 spectrofluorimeter was used to carry out steady-state luminescence measurements of ZnO. Time-resolved luminescence measurements of ZnO nanoparticles were made using the newly set femtosecond luminescence up-conversion spectroscopic technique briefly described elsewhere. The upconversion system used in our experiments was obtained from CDP Instruments, Inc., Russia. Specifically, the system used third harmonic generation from the mode-locked broad band Ti-sapphire laser (Spectra Physics,
The present measurements were carried out with 280 nm excitation (fundamental of Ti:sapphire was set at 840 nm). Polarization of the excitation beam for the magic angle luminescence and anisotropy measurements was controlled using a Berek compensator and the sample was continuously rotated with a rotating cell of 1 mm thickness. Horizontally polarized luminescence emitted from the sample was up-converted in a nonlinear crystal of $\beta$-barium borate using a pump beam at 800 nm, which first passed through a variable delay line. Instrument response function (IRF) was measured using the rise time of several dye molecules. Fitting the rise time of the luminescence traces gave a sigma value of ~290 fs. Parallel and perpendicular decay traces were obtained from which the magic angle luminescence decay was calculated from these traces. Fitting of the luminescence decay traces were carried out with DecFit software. Spectral resolution was achieved using a double monochromator and photomultiplier tube. The excitation average power varied, but was around 10 ± 0.3 mW. No degradation of the sample was observed as the traces overlapped after each repetition.

6.2.2. Synthesis of ZnO/GO Nanocomposites

The procedure of this experiment can effectively be split into three parts. The synthesis of GO, the synthesis of ZnO, and the fabrication of ZnO/GO nanocomposites. GO was synthesized using Modified Hummer’s Method. Briefly, 5 g of pre-bought graphite powder was put in a round bottom flask. To this, 4.5 g of KNO$_3$ and 169 mL of H$_2$SO$_4$ was added. The flask was placed in an ice bath. While this mixture stirred, 22.5 g of KMnO$_4$ was added over 1 hour. After 2 hours, the mixture was removed from the ice bath and left to stir for 5 days. The resulting black, viscous liquid was added to 500 mL of 5 wt% H$_2$SO$_4$ aqueous (aq), while stirring was continued. After 2 hours, 15 g of 30 wt% H$_2$O$_2$ was added and the mixture was stirred for another 2 hours. This resultant mixture was then washed with a 500 mL aqueous solution of 3 wt% H$_2$SO$_4$ and a 500 mL
aqueous solution of 0.5 wt% H₂O₂. In 2 days, the solution formed a precipitate. This washing process was repeated 10 times over 20 days, finally resulting in a dark yellow, thick liquid. This liquid was then centrifuged to remove the solid GO particles from the acidic solution which can be re-dispersed in water after sonication. The synthesis of ZnO nanoparticles were described in Chapter 3. The carboxylic acid groups of GO bind to ZnO nanoparticles and the mixing of ZnO nanoparticles with GO and stirring for 2 hours produced ZnO/GOnanocomposites. Characterization of GO/Zn) nanocomposites were carried out with UV/Vis, luminescence and TEM measurements.

6.3. Results and Discussion

6.3.1. Sensing of DO by ZnO

The synthesized ZnO nanoparticles were characterized by optical absorption and steady-state luminescence spectra. The band-edges of optical absorption spectra were used to determine the size of ZnO nanoparticles. A preliminary experiment was carried out for sensing DO by ZnO nanoparticles. Shown in Figure 6.1 are steady-state luminescence spectra of 3.8 nm ZnO nanoparticles as synthesized, purged with nitrogen and re-purged with oxygen. As observed earlier, the ZnO nanoparticles showed two luminescence peaks, one near the band edge and another in the visible region which is termed as trap-state luminescence. N₂ purging leads to the removal of DO. It can be observed from Figure 6.1 that with N₂ purging, a decrease in trap-state luminescence was observed along with an increase in trap-state luminescence. This result shows that a decrease in DO concentration lead to a decrease in trap state luminescence. This result concurs with the hypothesis that the trap state luminescence arises out of the electrons trapped at the oxygen filled vacancies recombining with deep trapped holes. With the removal of DO, these trap states are absent quenching the trap state luminescence and increasing the band edge.
luminescence as this pathway to trap states are eliminated. With O$_2$ purging, a decrease in band edge luminescence and an enhancement of trap-state luminescence was observed. (Figure 6.1) These results prove the hypothesis that ZnO nanoparticles can be able to sense DO efficiently and sensitively with a turn-on visible luminescence.

**Figure 6.1** Steady-state luminescence spectra of 3.8 nm ZnO nanoparticles showing influence of oxygen purging and nitrogen purging

### 6.3.2. Effect of ZnO Nanoparticle Size on the Sensitivity to DO

A systematic study was carried out to monitor the effect of N$_2$ purging on ZnO luminescence of two particle sizes and shown in parts A and B of Figure 6.2. It can be observed from Figure that the trap state luminescence has decreased while an increase in band-edge luminescence was observed and is similar to what was observed in the preliminary results.
The luminescence spectra for 3.4 nm and 3.9 nm sized ZnO nanoparticles have been compared by investigating the effects of nitrogen purging from their band edge and trap state luminescence values relative to their sizes. As expected from the preliminary experiments, there was significant quenching of the trap state luminescence and an increase in the band edge luminescence was observed for both samples. To further investigate the nitrogen purging on the difference ZnO nanoparticles sizes we have compared the band edge and trap state luminescence intensities for different sized ZnO nanoparticles. Each sample was purged with nitrogen with equivalent time intervals and pressure. After the luminescence scans, the band edge and trap state luminescence intensities were taken from the corresponding emission spectra, from which the intensity values were plotted against the time of nitrogen gas purging. Parts A, B and C of Figure 6.3 show the plots of normalized band edge, trap-state and ratio of trap-state to band edge luminescence as a function of the time of N₂ purging. It can be observed from Figure 6.3 A that there is an increase in band-edge luminescence for all sized ZnO nanoparticles with increase in
nitrogen and also there is a decrease in trap-state luminescence of more than 60% (Figure 6.3B). The ratio of trap-state to band-edge luminescence has shown maximum influence where in 90% decrease was observed with increase in N₂. However, the effect of particle size on the sensitivity was found to be limited. This might be because of the fact that the size range studied was small and the trap state densities might be not that much indifferent.

Figure 6.3 Band edge luminescence of ZnO nanoparticles and B) trap state luminescence plotted by nitrogen gas concentration. C) Intensity ratio showing no extreme effect relative to the size of the nanoparticles
6.3.3. Influence of Synthetic Conditions of ZnO on the Sensitivity to DO

The sizes of nanoparticles seem to have little influence on the sensitivity to DO. As observed in chapter 3, surface states can be varied by changing the synthetic conditions of ZnO. We have synthesized ZnO nanoparticles in IpOH, EtOH and DMSO and studied the sensitivity of these nanoparticles to DO. For a comparison, sensitivity measurements were carried out for same sized nanoparticles with nitrogen purging. Shown in parts A, B and C of Figure 6.4 are the normalized band-edge, trap-state and trap-state to band-edge luminescence intensities as a function of time of nitrogen purging. Here again, the effect of synthetic conditions seems to be negligible. However, the main point is that all nanoparticles have sensitivity to DO although the synthetic conditions seem to have little influence.
All the measurements have shown that ZnO nanoparticles can work as turn-on luminescent DO sensors. The mechanism is based on the fact that the trap-state luminescence arises out of electrons trapped in oxygen filled vacancies recombining with deep trapped holes. If there is no oxygen to fill the vacancies, the trap-state luminescence is quite low. However, it would be difficult to make luminescent optical sensors for DO with them as the trap-state luminescence can be reduced when they are deposited on substrates. Thus, we have attempted to find suitable substrates that can make able ZnO to sense DO better and that can be used to make devices out of them.

### 6.3.4. ZnO/GO Nanocomposites as DO Sensors

One of the highly investigated substrates in recent years is Graphene. Graphene, a reduced derivative from graphene oxide (GO), has received much attention due to its applicability to enhance gas sensors. Even GO was found to be a good substrate for sensing as well as catalysis. GO possess carboxylic acid functional groups that can covalently bind to ZnO nanoparticles. Thus, in this study, we propose to use graphene oxide (GO) as a substrate to bind to ZnO nanoparticles. GO exhibits excellent electrical and thermal conductivities, it possess stable mechanical
disposition, is soluble in water, and possesses many surface functional groups that can bind to ZnO. We have synthesized ZnO/GO nanocomposites and characterized them with TEM measurements. (Figure 6.5) TEM few ZnO nanoparticles are not bound to GO.

![Figure 6.5](image)

Figure 6.5 (A) TEM images of ZnO nanoparticles at 80,000 times with an average of 3.7 nm particles and B) ZnO/GO nanocomposites with an average length of 5 μm GO sheets with the black dots ZnO nanoparticles percolated on the GO sheets

Before carrying out the sensitivity measurements for ZnO/GO nanocomposites, the sensitivity of GO alone to DO were carried out. Shown in Figure 6.6 A are the steady-state luminescence spectra of GO alone, with nitrogen and oxygen purging. The results show that the effect of DO on GO is minimal as it does not interact with GO at all. A preliminary study was carried out with ZnO/GO nanocomposites for sensing DO. It is observed from results (Figure 6.6B) that the trap-state intensities were quite low with ZnO/GO nanocomposites probably due to the interaction of GO with ZnO. However, the effect of nitrogen and oxygen are quite evident and / ZnO/GO nanocomposites were able to sense DO very efficiently. With nitrogen purging, both band-edge as well as trap-state luminescence intensities were quenched. However, with oxygen
purging, trap-state luminescence has increased, suggesting that ZnO/GO can act as good DO sensors.

Figure 6.6 Sensitivity of (A) GO and (B) ZnO/GO to dissolved oxygen. Nitrogen purging removes dissolved oxygen while oxygen purging recovers it

6.3.5. Ratiometric Sensing of DO

One of the best ways to sense DO with ZnO is by using the ratio of trap-state to band-edge luminescence intensity that has shown maximum effect. The intensity ratios (trap state luminescence over band edge luminescence) of the ZnO nanoparticles and ZnO/GO nanocomposites both possess the oxygen gas sensing properties needed for them to be presentable candidates for turn-on luminescent operational sensors. However, when equating the ratiometric sensing proficiencies, an outstanding variation between the two systems is distinctly apparent. (Figure 6.7) Comparing the unpurged values, the ZnO/GO nanocomposites luminescence ratios are twice as intense. With the incorporation of nitrogen the ZnO/GO are about four times the value from that of ZnO nanoparticles alone. When we integrate oxygen gas into the systems we see both the 1-min and saturation purging samples for ZnO/GO possess significantly higher ratiometric
intensity values just under 1 times as much, compared to bare ZnO. After assessing the values, we can see an occurring trend with the ZnO/GO nanocomposites establishing a more visible response to the oxygen gas in the system. This exponential enhancement could play an imperative role in later properties that are involved in sensitivity, enhancement, and the sensitivity to DO.

![Ratiometric sensing of Oxygen](image)

**Figure 6.7** Ratio of trap-state to band-edge luminescence intensities as a figure of merit for sensing DO

### 6.3.6. Mechanism of DO Sensing

Femtosecond luminescence measurements were carried out to monitor the dynamics of band-edge luminescence with and without purging nitrogen. Shown in Figure 6.8 are the luminescence decay traces with and without purging for ZnO samples after excitation at 266 nm. The results show that the band-edge luminescence dynamics is slowed down with nitrogen purging suggesting the low rate of trapping occurs when the oxygen is not filling the vacancies.
On the other hand, band-edge luminescence dynamics was found to be quite faster for ZnO/GO compared to ZnO alone suggesting an interaction of ZnO with graphene oxide probably arising out of charge-transfer interaction. The results of DO sensing have shown that ZnO and ZnO/GO are good candidates for sensing DO. The ratiometric sensing have shown that ZnO/GO are better than ZnO alone indicating that GO is not just a substrate but also enhances the sensitivity by interacting with ZnO nanoparticles. The mechanism of DO sensing by ZnO/GO is depicted in Figure 6.9. ZnO nanocomposites alone are responsive to the presence of oxygen gas as the trap state luminescence is quenched and the defect states relax non-radiatively giving rise to the band edge luminescence. What separates the ZnO/GO nanocomposites from the ZnO is the electron transfer from ZnO to GO which reduced both trap-state and band-edge luminescence initially. Upon the addition of oxygen, the electron transfer from ZnO to GO is not favored; rather it traps to oxygen filled vacancies giving rise to trap-state luminescence.
6.4. Conclusion

The main objective of this study is to probe whether ZnO nanoparticles can be used as turn-on luminescent sensors for DO. The results have shown that ZnO nanoparticles can act as good DO sensors with turn-on trap state luminescence. With the removal of oxygen, trap-state luminescence is quenched while an enhancement of band-edge luminescence was observed. However with the addition of oxygen, an increase in trap-state luminescence was observed with a decrease in band-edge luminescence intensity. Femtosecond luminescence measurements have shown an increase in band-edge luminescence decay lifetime with the removal of oxygen via nitrogen purging. The mechanism was attributed to the reduced oxygen filled vacancies when oxygen was removed, leading to lower trap-state luminescence. When oxygen is present, the oxygen-filled vacancies increase enhancing the trap-state luminescence intensity. This study has shown that ZnO nanoparticles can act as turn-on luminescent sensors for DO. ZnO/GO
nanocomposites were synthesized to enhance the sensitivity to DO. The measurements have shown enhanced sensitivity to DO when ratiometric sensing (ratio of trap-state to band-edge luminescence) is considered. The enhanced sensitivity was attributed to the electron transfer interaction of ZnO nanoparticle with GO. With the addition of oxygen, electron transfer is less favored over trapping to oxygen-filled vacancies enhancing the trap-state luminescence. In this way our results have shown that ZnO, ZnO/GO nanocomposites can act as turn-on luminescent DO sensors.
6.5. Summary of Chapter 6

- Dissolved oxygen (DO) is one of the important analyte whose levels are to be determined for the sake of many applications such as aquatics, pharmaceuticals, oil spills etc. Current optical methods work on the principle of quenching of luminescence with oxygen.

- The goal of the work is to develop turn-on luminescent sensors based on the luminescence from ZnO nanoparticles.

- The results have shown that the trap-state and band-edge luminescence of ZnO are sensitive to DO with an enhancement for trap-state luminescence and quenching for band-edge luminescence. In this way, ZnO nanoparticles work as turn-on luminescent sensors for DO.

- The mechanism was attributed to the fact that the trap-state luminescence in ZnO nanoparticles arises out of the electrons trapped at oxygen filled vacancies recombining with deep trapped holes. In the absence of oxygen, no radiative trap states and the trap-state luminescence is lower while the band-edge luminescence gets higher because of reduced trapping.

- ZnO/GO nanocomposites were successfully synthesized and characterized and they have shown greater effect with ratometric sensing of DO.

- The mechanism of sensing was attributed to electron transfer from ZnO to GO in the absence of oxygen giving rise to reduced trap-state luminescence while the addition of oxygen favors trapping over electron transfer and thereby enhancing the trap-state luminescence.
6.7. References


CHAPTER 7

SUMMARY AND OUTLOOK

7.1. Overall Summary

The following is a summary of the objectives, conclusions, and the extensions that can be formulated from each of the projects studied.

The overall focus of the presented dissertation is to understand the charge carrier dynamics of bare surface modified semiconductor nanoparticles. The dynamics of charge carriers in semiconductors can be used in applications for nonlinear optical materials, solar cells, optical diodes, bio-medical tools and various sensors. Semiconductor nanoparticles possess many properties and their optical properties are well investigated and are implemented in several applications. The semiconductor nanoparticles are special due to quantum confinement effect that are very different from their bulk counterparts. Another contributing factor to the high energy of the semiconductor nanoparticles would be due to their greater surface to volume ratio. Optical properties of semiconductor nanoparticles are very important for their applications in photocatalysis, solar energy conversion and nonlinear optics.

Although enormous research as focused on the II-VI semiconductor nanoparticles, corresponding studies on ZnO and TiO$_2$ nanoparticles is limited. The research focus of the dissertation is to understand the charge carrier dynamics of these nanoparticles with an emphasis on improving the charge separation. The objective of this dissertation are understand: (i) the band edge luminescence dynamics in bare ZnO nanoparticles, (ii) probe the charge transfer excitons in surface modified
TiO$_2$ nanoparticle and (iii) understand the charge transfer dynamics in chromophore functionalize TiO$_2$ nanoparticles.

In the chapter 3 we wanted to explore the influence of the size on the charge carrier relaxation dynamics of band edge luminescence dynamics in bare ZnO nanoparticles. The investigations of the luminescence dynamics has implications in their optical applications of catalysis, sensing, and light harvesting. In the case of bare ZnO nanoparticles, both surface defect states as well as size can influence the band edge luminescence dynamics. To recognize which pathway dominates the band edge luminescence dynamics, measurements were carried out on ZnO nanoparticles synthesized in different methods. The three methods used were ZnO in IpOH (NaOH as the base), ZnO in EtOH (LiOH as the base) and ZnO in DMSO (NH$_4$OH the base). All the synthetic methods were able to give different sized ZnO nanoparticles and the sizes were determined from the onset of absorption correlating it to Brus’s equation relationship. All ZnO nanoparticles have shown band edge luminescence as well as trap state luminescence that was expected as the ZnO nanoparticles were not passivated. The band edge luminescence dynamics was monitored for the first time for ZnO nanoparticles that was possible from luminescence upconversion technique with 266 nm excitation. The luminescence decay traces were fitted with multi-exponential decay components and average lifetimes were obtained. The average lifetimes with size have shown that as the size is increased, the lifetimes have increased. However, the ZnO in DMSO has shown significantly faster lifetime with same size nanoparticle and thus size alone was unable to explain the charge carrier dynamics. To comprehend better, a figure of merit for understanding the rate of trapping was realized from the intensity of trap state to band edge luminescence. There is a good correlation between the average lifetimes and the intensity ratio
suggesting that the rate of trapping dominates the band edge luminescence dynamics in ZnO nanoparticles.

Summarizing chapter 4, the charge carrier relaxation dynamics in surface CT modified TiO$_2$ nanoparticles was studied with femtosecond time-resolved fluorescence and transient absorption spectroscopy. The overall objectives for this study are to probe the influence of donor/acceptor strength on the charge carrier dynamics in catechol and salicylic acid modified TiO$_2$ nanoparticles as well as to understand the influence of surface morphology on the charge carrier dynamics. Different catechol derivatives were studied namely MetCat, Cat, CN-Cat and NO$_2$-Cat with increasing strength of acceptor on catechol. Optical absorption measurements have shown that all Cat and Sal derivatives modify the surface of TiO$_2$ via the formation of LMCT complex with surface Ti atoms. Increasing the acceptor strength on catechol lead to stronger CT complex with TiO$_2$. The Femtosecond time-resolved luminescence measurements have shown ultrafast ICT emission from all small molecule derivatives sensitized TiO$_2$ and with emissions arising from localized excitations. The CT emission decay is a result of both charge delocalization and geminate recombination. Cat and NH$_2$-Cat have shown instantaneous ICT emission decay that is assigned to charge delocalization from the excited CT state. However, with an increase in acceptor strength, the emission was slowed down as the delocalization into TiO$_2$ is an uphill process.

The transient absorption measurements of Cat/TiO$_2$ have shown the presence of an excited CT state which decays with different time scales than charge recombination. However, no such evidence of excited CT was found for Sal/TiO$_2$. This is attributed to the fact that Cat forms stronger CT complex with defect Ti$^{3+}$ states while Sal forms complex with Ti$^{4+}$ states on the surface of TiO$_2$ nanoparticles. With increased donor strength on Catechol, the charge separation was higher
while increasing the acceptor strength on catechol, decreased the efficiency of charge separation but increased the decay contribution from the excited CT state. The results show that donor substituted catechols are suitable candidates to achieve better charge separation. Interesting charge-carrier dynamics was observed for Cat/TiO$_2$ in thin films. This systems in thin films has shown no evidence for excited CT states however, the dynamics is dominated by instantaneous charge separation and slow charge recombination. This is rationalized based on the absence of defect Ti$^{3+}$ states in thin films. The results show that it is possible to achieve greater charge separation with CT modified TiO$_2$ nanoparticles with appropriate choice of substituents and surface morphologies.

In chapter 5 we were able to probe and understand the influence of surface CT modification on charge-carrier dynamics of sensitizer/semiconductor nanoparticle systems from chromophores with CT forming anchoring groups (AnthCat and PyrCat) which were synthesized via Schiff-base condensation. The corresponding spectra revealed that the excited state dynamics of AnthCat and PyrCat were dominated by ultrafast decay components arising out of charge-transfer from Amine moieties to the core of dye molecules. On the other hand, when the dyes are attached to TiO$_2$ nanoparticles, efficient charge injection to the surface of TiO$_2$ is observed. Femtosecond fluorescence upconversion and transient absorption measurements have shown the evidence for ultrafast charge injection with contribution from both Type I and Type II injection pathways. Still, components for charge delocalization into TiO$_2$ were observed as well. The charge delocalization components for both dyes are more evident in solution than on thin films. The charge recombination dynamics was established to be multi-exponential with significant component of greater than 1 ns. It was realized that dye/CT-semiconductor nanoparticles also can lead to efficient charge separation. Interestingly, long-lived charge separation is higher with thin film samples
compared to solution phase. The long-lived charge separation in thin films is attributed to lower
density of trap states in thin films when compared to nanoparticles in solution. Overall, the results
show that CT forming anchoring groups can be used for solar cell applications and they also give
long-lived charge separation similar to that of carboxylate anchoring groups.

For chapter 6 it was realized that ZnO nanoparticles can be used as turn-on luminescent
sensors for DO. The results have shown that ZnO nanoparticles perform as decent DO sensors
with turn-on trap state luminescence. With the removal of oxygen, trap-state luminescence is
quenched while an enhancement of band-edge luminescence was observed. It was observed that
with the addition of oxygen, an increase in trap-state luminescence was observed with a decrease
in band-edge luminescence intensity. The femtosecond luminescence measurements have shown
that there is an increase in band-edge luminescence decay lifetime with the removal of oxygen via
nitrogen purging. The mechanism for this turn-on luminescence system was attributed to the
reduced oxygen filled vacancies when oxygen was removed leading to lower trap-state
luminescence. With oxygen, the oxygen filled vacancies increase enhancing the trap-state
luminescence intensity. This study has shown that ZnO nanoparticles can act as turn-on
luminescent sensors for DO. Furthermore, ZnO/GO nanocomposites were synthesized to enhance
the sensitivity to DO. The measurements have shown enhanced sensitivity to DO when ratiometric
sensing (ratio of trap-state to band-edge luminescence) is considered. The enhanced sensitivity
was in these systems was ascribed to the electron transfer interaction of ZnO nanoparticle with
GO. With the addition of oxygen, electron transfer is less favored over trapping to oxygen filled
vacancies enhancing the trap-state luminescence. In this way our results have shown that ZnO,
ZnO/GO nanocomposites perform as worthy turn-on luminescent DO sensors.
7.2. Future Outlook

Overall this research is relative to the phenomena of charge transfer dynamics in nanomaterial systems as it has been explained throughout this dissertation. Furthermore, the overall motivation of this research was to design and develop better semiconductor nanomaterials for various applications which include components of nonlinear optical materials, solar energy conversion, and sensor devices by monitoring the charge transfer in various chemical systems. These chemical systems consisted of bare ZnO nanoparticles, surface modified and surface functionalized TiO$_2$ nanoparticles and ZnO/GO architectures. We were able to define that luminescence of the ZnO nanoparticles is dominated by the extent of the trap state luminescence and not the size of the particles and that the band edge luminescence minor influence on them. On the other hand, we have shown and studied its applicability in ZnO/GO nanocomposites as turn-on luminescent devices for the detection of DO. In addition, surface modified small molecule and catecholate adsorbed to TiO$_2$ nanoparticles have demonstrated that binding properties significantly affect the charge transfer time scales and directions within electron injection and recombinant trails.

Overall the ideal for this research is to understand and further define the needed fundamental properties of charge transfer mechanisms. Although femto-second spectroscopy was used to map some of these properties it would be interesting to incorporate them into an additional analytical study using 2PA cross section to see if these TiO$_2$ systems are useful for nonlinear optical materials. Also, electrochemical measurements may reveal supplementary properties about them. Future experimentation may entail the use of a dye molecule to ZnO/GO nanocomposites likewise with TiO$_2$. As with the ZnO/GO nanocomposites it would
interesting to see the uniformity of the ZnO nanorods with the graphene oxide nanosheets. Furthermore, there is a continuing effort to produce stable ZnO nanocomposite thin films.