Ultrafast Spectroscopy and Energy Transfer in an Organic/Inorganic Composite of Zinc Oxide and Graphite Oxide

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Ultrafast Spectroscopy and Energy Transfer in an Organic/Inorganic Composite of Zinc Oxide and Graphite Oxide

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and

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A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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ABSTRACT

This thesis describes the ultrafast processes in a hybrid organic/inorganic composite of Zinc (hydr)oxide and graphite oxide. The zinc phase is a large bandgap semi-conductor metal oxide with broadband visible emission from 430 - 600 nm caused by large density of surface and defects that act as trap states within the bandgap of the metal oxide. These surface states are observed to be brightly luminescent with long lifetimes. Steady state absorption, emission and Raman scattering provide a first look into the nature and effects of the hybridized defect states. Different luminescent structures are observed when the energy of excitation lies below the fundamental band edge of the zinc phase even though there is no structure in the absorption spectra caused by these intermediate states. This is analyzed with tunable laser excitation energy and the appearance of the blue-shifted emission with sub band gap excitation energies is attributed to a range of defect levels and the charge transfer state near the band edge of ZnO that becomes unaccessible under resonant absorption due to band bending effects of the excited electrons in the conduction band. In the time domain, the composite system GO shows very long and reversible nanosecond decay characteristics of the GO and shortened decay processes in the zinc phase. It is hypothesized that the overlap of the defect states of the two materials leads to strong interaction of the dense defect states of each material. To analyze this, spectrally and polarization resolved ultrafast decays are compared between the components in neat form and in composite form to give details on the ultrafast transfer/decay processes. The lifetimes of the different spectral regions of the emission show multi-exponential behavior that can be
grouped into three energy regions: the zinc phase exciton, the charge transfer/surface state overlap emission, and the defect level emission. Comparison of each region as a function of excitation energy build up a energy landscape of the states within the composite to determine the energy transfer processes between the zinc phase and the graphite oxide phase.
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Freedom is on the Horizon...

Let’s start walking ‘til we get there.

1

Optics and Spectroscopy

1.1 Introduction

This thesis studies the spectroscopy of a newly synthesized compound of Zinc Oxide with Graphite Oxide made by the Chemistry group of Professor Teresa Bandosz. The study is to identify signatures and the nature of the charge or energy transfer that are unique to this compound with graphite oxide. Steady state absorption and emission spectroscopy develops a picture of the energy
landscapes and transfer pathways in the material by comparing the individual components and neat forms of the composites. Vibrational spectroscopy shows the complex bonding of the GO with the ZnO and resonance signatures of the composite. The kinetics of the energy transfer processes are probed with ultrafast spectroscopy with tunable excitation across the fundamental bandgap of the materials. A number of features are identified that are modified from the spectral properties of the parent compounds as well as unique signatures found only in the composite materials. The broadband visible emission shows a complex change as the energy of excitation crosses the gap of ZnO and strong visible emission is stil observed with energies well below the fundamental gap of ZnO. These are described to be from a range of defect states of the parent compounds and interface states of the Zinc Oxide and the Graphite Oxide. The nature of the strong emission with sub band gap energy is considered as a mediating chanel for the energy transfer process from the Zn phase to the GO. The thesis is divided into five chapters. Chapter 1 is an overview the field and basic optics and physical processes involved, and an overview of experimental spectroscopic techniques. As this thesis work is an experimental investigation, much detail will be given to the techniques used to undertake the measurements. Although as a physicist we are not technicians, we must understand and develop our techniques in order to obtain faithful and rich experimental information. The fundamental properties of light and its uses for experimental work is discussed as well as basic optical principles used throughout this work. Chapter 2 contains the linear spectroscopy of the materials such as absorption, emission and Raman spectroscopy. Chapter 3 discusses the ultrafast
emission of these materials with near UV excitation of 266 nm obtained from a frequency quadrupled picosecond laser. The spectra were decomposed into three broad wavelength ranges corresponding to the zinc oxide optical gap, a defect emission band in the visible and longer wavelength red emission associated with the graphite oxide. Chapter 4 develops the ultrafast experiments described in chapter 3 into multidimensional spectroscopy. A femtosecond tunable laser system is constructed for tunable excitation wavelengths starting at 350 nm and extending into the near infra red. Finely incremented laser excitation spectra are made of the composite materials to investigate the luminescent properties for excitation energies tuned over the fundamental gap of the Zinc Oxide. The ultrafast luminescent signals are decomposed in the excitation energy, emission energy, time and polarization dimensions. The lifetimes across the emission spectra are compared for different excitations, and those excitations near the gap and below are analyzed in consideration of hybridized interface states that can be activated/deactivated with excitation leading to conduction band electrons in the Zinc phase.

1.2 Background of the Field

The physical processes concerned in this thesis study cover several fields of current science. The inorganic phase of these composites is a well studied metal, along with its oxides, for the purposes of light sensitization and light driven chemical and physical processes. The organic phase, Graphite oxide, is an old material but has come into the forefront of science recently due to the discovery of exotic properties of nanoscale carbon. Individually these phases are found
to have new properties once brought down to nanoscale size and the composite of the two should uncover new physical interactions and hybridizations of the parent properties. Inorganic materials often benefit from long term stability, high energy excitations that support powerful chemical reactions and the appearance of energy bands that can promote conductivity across long distances. Zinc Oxide has a fundamental gap in the near UV region of the spectrum at 380 nm and therefore on its own would not be very photoactive for much of the solar spectrum. Graphite oxide on the other hand is remarkable photoactive in the visible range of the solar spectrum and the vast number of bonding configurations afforded by carbon atoms makes it a very versatile material. Therefore the hybridization of these materials could offer a mixture of high energy stable excitations as well as broadband reactivity with visible light and highly versatile chemical functionalization with an organic phase. The question arises then, what is the nature and the effect of hybridization of these materials and are there any emergent properties unique to the composite?

Nano forms of Zinc and Carbon have been developed by a number of labs in the past few years [1, 2, 3, 4, 5, 6, 7]. However, in many of the work to date on composite materials of Zn and carbon, the final product is usually one form functionalized by the other, i.e. ZnO nano rods decorated with GO, or GO sheets decorated with Zn nanoparticles. In these systems, one would anticipate a type of energy or electron transfer that is familiar to the fields of fluorescence resonance energy transfer (FRET) or sensitization of GO for light activated photochemistry using the high energy states of the Zn inorganic phase. Some of the signatures of FRET would be a delayed fluorescence of the lower energy
emission or observable rise times in the low energy emission that correlates to
the decay of the high energy emission. In contrast, the ZnGO composites con-
cerned in this thesis, which were synthesized by the Bandosz group, arguably
have a different physical framework of the composite. There is no evidence
of sensitization of one phase by the other which would indicate FRET, and
the observed optical signals are found to be mostly irreversible which excludes
permanent electron transfer or redox reactions between the Zn and GO[4].
In this case the GO and Zn phases are not electronically isolated and intra-
molecular interaction is assumed versus inter-molecular. The framework of this
composite leads to a highly porous material that increases the adsorption and
sensing properties[3, 5, 6]. In addition the porous nature should be beneficial
for dye/quantum dot sensitization for photovoltaics, if the porous nature does
not decrease the conductive paths for electrons. Likely the scattering of elec-
trons in a porous structure would be greater than the increase in conductivity
making current carrying devices with these composites difficult. Nonetheless,
the defect levels in these composites should play a critical role in the physical
properties since the new properties are dependent on the nanoscale. At the
moment, 2% seems to be an optimal level of GO in this composite[5, 6]

1.3 Fundamentals of Light

Light is radiant electromagnetic energy. The salient properties of light are its
frequency (energy or wavelength), polarization, and phase. The frequency and
wavelength are inversely related via the wave equation \( c = \lambda \nu \) with \( c \) the speed
of the light propagation, λ the wavelength and ν the frequency of oscillation. The polarization of the wave is taken as the direction of the stress of the electronic component of the field. Maxwell’s equation in simple form for a freely propagating field, \( \vec{E} \times \vec{B} = -\vec{k} \), shows that the magnetic component of the field is uniquely defined perpendicular to the electronic component and also to the propagation direction, the three vectors forming an orthogonal triad that spans the dimensional space, therefore the magnetic component usually need not be explicitly specified. The phase of the light is a temporal phenomenon that is observed when two or more waves combine. If there is a non random phase relationship between the combining waves then the oscillation components of the waves are observed to interfere leading to enhanced or diminished intensity at the point of combination. The energy of the radiant field is described quantum mechanically as the energy of a harmonic oscillator \( E = h\nu \) where \( h \) is Planks constant = \( 6.626 \times 10^{-34} \). Visible light has a wavelength range approximately between 350 nm (violet) to 800 nm (red) corresponding to 3.5 to 1.5 electron volts (eV). Other familiar forms of light are radiant heat (infra-red light), X-rays, and radio waves. The range of frequencies of freely propagating light is from 0 (DC or zero field) and no classical upper bound. Though frequencies above the Planck length become ill-defined as the wavelength is shorter than this lower quantum limit. Another salient feature of a freely propagating field is that it carries zero rest mass. Classically and quantum mechanically the momentum of a massive particle is related to its energy as \( E = \frac{p^2}{2m} \). The dispersion curve showing energy vs momentum for a massive particle is thus a parabola offset by the rest mass of the particle as seen in figure 1.3. Light on the other
1.4 Ray Optics and Imaging

Ray optics is important to consider in all experiments for several reasons. Signal collection intensity is maximized with optimal focusing which reduces the duration of the experiment and thus reduces irradiation effects/damage and
improves signal to noise ratio. Depending on the detection system used, improper focusing can lead to modified or false spectral features. Also, with detection systems using a narrow aperture for analysis such as a spectrometer or streak camera, the resolution of the measurements are set by the size of the aperture and therefore maximal resolution can be obtained with tight focusing into the collection slit. Below are the basic principles of ray optics and imaging that are useful in spectroscopic measurements.

The optical diagram is comprised of a principle axis which is usually an imaginary line through the center of the optical elements and the sample under study. Generally a point source is considered as the starting image from the
sample, either as scattered or luminescent light. The focal point of a lens is conjugate to a point at infinity for a point source and vice versa as shown in figure 1.4. Another way to understand this is that the propagation of light is time reversal invariant and so the system can be reversed which gives the same results as using the principle rays.

Figure 1.3: Ray diagram of a point source and the conjugate scenario where rays parallel to the optic axis are focused to a point.

A lens can be considered as a mapping of angles to points where the angular map is scaled by the focal length of a lens. This concept becomes very helpful when considering the image formed on a detector after a grating is used. In this case, there “extended object” is not well defined and what is more important is the angular distribution of the rays. As a simple example, consider the image formed by a lens of a double slit interference pattern. It is not of interest to image the finite sized double slit but rather to focus the interference pattern generated by the double slit arrangement. The use of principle rays can easily define the image formed. Considering the rays through the focal point which will exit parallel to the axis, and the ray through the center which will travel
undeviated, the final image is well defined and depends only on the focal length of the lens. In the far field, the distance from the double slit to the lens does not change the image so long as the same rays are able to enter the lens at different distances. Grating spectrometers, etalons and Fabry-Perot systems all depend on the imaging of an angular distribution rather than a point source.

![Diagram of a lens and its focal point](image)

Figure 1.4: The image formed by a lens of an angular distribution, for example of an interference pattern from a double slit. A second, non-existent ray drawn parallel to a principle ray will define the focal point of all other rays parallel to this direction.

## 1.5 Spectroscopy

The major experimental method of this work is based on optical spectroscopy. In short, any experiment will measure one or more of the salient properties of light when interacting with a material. Linear or conventional spectroscopy uses continuous or quasi continuous probing light to analyze a material. Ultrafast spectroscopy uses short pulses of light for temporal resolution and non linear experiments with high intensity afforded by the ultrafast pulse of light.

In most of the following linear spectroscopic measurements a spectrometer
system is used to analyze a bandwidth of light passing through (absorption) or radiating from (fluorescence) a test material. The basic working principle of a spectrometer can be explained very easily with the concepts of geometrical optics and mappings. The light to be analyzed is imaged onto the entrance slit of the spectrometer. The final result will be a spectrally resolved image of the entrance slit onto the exit focal plane. For this reason a narrow slit width is optimal for best spectral resolution at the focal plane since each of
the constituent wavelengths will be imaged onto the exit focal plane with a width equal to the width of the slit in a 1:1 magnification system. A focusing element collimates the incident light and passes it to a grating that diffracts the light. This is a mapping of the energy of the light into angular space. A second optical element images this angular image which by the principles of optical focusing elements maps angles to points. Therefore the overall mapping sends energy (wavelength) values to points along an axis. This axis can be read out with a CCD or point by point with a 1-D detector such as a photo-diode or photomultiplier. In general, matching of the f-number of the system will achieve optimal resolution as this utilizes the maximum size of the diffraction grating. The usual trade-off is that a short focal length lens imaging onto the slit will produce a smaller spot size but thus leads to a larger divergence of the light inside the spectrometer and some light is lost. A longer focal length lens will be easier to properly illuminate the collimating mirror inside the spectrometer but gives a larger spot size at the entrance slit. If the incident light can be collimated to a small spot before being focused onto the entrance slit, a short focal length lens can be used to achieve a small spot on the slit and the divergence inside the spectrometer can fully illuminate the collimating mirror. For example, if a 5 mm collimated beam is focused onto the entrance slit with a 5 cm lens, then after 75 cm the beam will expand to 15 times it’s size, or 75 mm which is near the size of most spectrometer optics.
1.6 Physical Processes Probed by Linear Spectroscopy

The energy landscape of a material can be probed with photons. Electronic states of a system can be probed by various forms of absorption and emission processes and structural details can be observed with inelastic light scattering. A transition from a state $i$ to another state of the system $j$ with energies $E_i$ and $E_j$ can be induced with an amount of energy $\Delta E = E_i - E_j = \hbar(\nu_1 - \nu_2)$.

Let $\Psi_i$ and $\Psi_j$ be the wavefunctions for states $i$ and $j$ defined as $H_o |\Psi_i\rangle = E_i |\Psi_i\rangle$ where $H_o$ is the systems Hamiltonian. The interaction with a photon can couple the two states, expressed as $\langle \Psi_j | V | \Psi_j \rangle$ where $V$ represents the interaction of the photon with the system.

Suppose the final state of the system, $\Psi$ to be a combination of states $i$ and $j$, $\Psi = a \Psi_i + b \Psi_j$ where $a$ and $b$ are functions of time. The states $\Psi_i$ have their own time evolution $e^{2i\pi\nu t}$. Schroedinger’s equation reads.

$$\frac{\partial}{\partial t} \Psi(r, t) = \frac{i}{\hbar} V \Psi(r, t)$$

Dropping the spatial terms for the moment and applying left multiplication by the final states leads to

$$\frac{\partial}{\partial t} \langle \Psi | \Psi \rangle = \frac{i}{\hbar} \langle \Psi | V | \Psi \rangle$$

Integrating the time variable and writing $\Psi$ as a combination of the initial states gives
\[ \langle \Psi | \Psi \rangle = \int_{-\infty}^{+\infty} \frac{i}{\hbar} \langle a\Psi_i + b\Psi_j | V | a\Psi_i + b\Psi_j \rangle dt \]

The left side is defined as non-zero if the system exists. If \( a \) and \( b \) commute with \( V \), i.e. \( aV = Va \) then

\[ \frac{i}{\hbar} \int_{-\infty}^{+\infty} a^2 \langle \Psi_i | V | \Psi_i \rangle + b^2 \langle \Psi_j | V | \Psi_j \rangle + ab \langle \Psi_i | V | \Psi_j \rangle + ba \langle \Psi_j | V | \Psi_i \rangle dt \]

The first and second terms integrate to zero since the only factor remaining is the time dependence of the input \( V \), i.e. \( \int e^{2i\pi \nu t} dt = \delta (\nu) \), \( \delta \) the Dirac delta function, leaving only the cross terms \( ab \langle \Psi_i | V | \Psi_j \rangle + ba \langle \Psi_j | V | \Psi_i \rangle \) The time dependencies lead to the integrals involving \( e^{2i\pi \Delta_{ij}} \) and \( e^{2i\pi \Delta_{ji}} \) where \( \Delta_{ij} \) is the difference in the frequencies of oscillation of the two states and \( \nu \) is the energy of the photon. The only way for the right side to not be identically zero and satisfy the left side of the equation is if \( \nu = \Delta_{12} \) or \( \nu = \Delta_{21} \). One case being for absorption of energy or a transition into the higher energy state, the other being emission of energy and a transition to the lower energy state.

### 1.6.1 Absorption and Emission Spectroscopy

The basic optical measurement involves absorption of a known frequency of light to determine the interaction of the system with that frequency. Generally, absorption spectroscopy involves electronic transitions. Upon absorption, the system can undergo a number of processes, and eventually can re-emit light of its own characteristic spectrum. Figure ?? describes a generic picture of the
energy levels of a system. The vertical axis is energy and the horizontal axis is a generalized co-ordinate which could be a bond length, bond angle, solvent reorganization energy, etc. For a semiconductor system the lower parabola is inverted to represent the opposite potential felt by holes and the horizontal axis becomes the momentum of the excitation. The parabolic curves represent an eigenstate of the system that is approximated by a harmonic confining potential for the electron. The horizontal lines represent the quantized vibrational levels of the system. Upon absorption of a photon, the electron undergoes a “vertical” transition, and absorption occurs when the vertical arrow reaches the upper energy level. In case (a), both the upper and lower energy levels have the same electronic potential with no shift along the horizontal axis. Therefore the minimum energy needed to excite the electron will be the same as the energy that the system can omit. In this case the absorption peak energy is the same as the emission peak energy. In the second case (b) the excited state manifold is shifted along the horizontal. Now the minimum energy needed to raise the electron from the lower level is less than the peak emission energy, called a Stoke’s shift. In the final case (c) there is no shift of the excited state manifold but rather a deformation. Here also it is possible to have a shift in the absorption energy and the emission energy.

After photo excitation into a higher energy state, the energetic electron usually undergoes vibrational relaxation by generating phonons in the molecular material. Phonon energies are in the 100 meV range. This decay process is few picoseconds and shorter in duration. In strongly polar materials with well defined transitions, a series of phonon sidebands may be observed in the ab-
sorption and emission spectra of the material, and usually a low temperature. No such sideband character was seen in the spectra of these ZnGO composites even though ZnO is a highly polar material. The next section discusses in detail the vibrational characteristic spectra of these materials. A crystalline material will have some degree on long range translational symmetry of the unit cell.

Figure 1.6: Jablonski diagrams showing three different scenarios of an absorption/emission process. The vertical axis is energy and the horizontal axis is a generalized co-ordinate usually considered as a structural potential caused by a reconfiguration of the electronic/nuclear wavefunctions. The horizontal lines within the potential are quantized vibrational energy levels within the electronic state. In a, the ground and excited state have identical potential energy surfaces and the absorption (vertical arrow) has the same energy as the emission. In case b, the excited state potential is offset in the co-ordinate direction so the maximum absorption is at a higher energy than the emission. In c, the excited state potential energy surface is more dispersive which can also lead to a shift in the emission energy.
that makes up the crystal structure. In this case the momentum of the excitation is well defined. Due to the translational symmetry of a crystalline lattice, the wavefunctions that exist on the crystal lattice will have simple Fourier transforms and the momentum wavefunctions will make up energy bands that exists within a finite region of momentum space. i.e. the Fourier transform of an infinite lattice of unit cells of size $a$ will have a momentum space (Brillouin zone) of extent $2\pi/a$. Additionally, because the electronic excitation is potentially mobile in an infinite lattice, the motion of the electron as well as the motion of the lack of electron, or hole, can be accounted for. The lack of the electron leaves a positively charged state. Considering the reaction of the electron and hole to an external electric field, the opposite charges will respond oppositely. Therefore the valence bands of are directed oppositely to the conduction bands in a semiconductor material. Figure 1.6.1 shows a generic electronic dispersion for a direct and indirect gap semiconductor. The vertical arrow represents an optical transition and the sideways arrow is a change in momentum which comes for the interaction with vibrations, or phonons.
Figure 1.7: Dispersion curve of electrons in a direct bandgap (left) and an indirect bandgap semiconductor (right). In the direct bandgap, the minimum energy difference between the conduction band and the valence band occurs at the same momentum value. The vertical red arrow is the smallest photon energy that generates an electron hole pair. In an indirect semiconductor, the minimum energy difference between the valence and conduction bands are not at the same momentum value and so the minimum energy absorption is be accompanied by a momentum scattering event, i.e., the absorption or emission of a phonon (sideways red arrow).
1.6.2 Raman Spectroscopy

Absorption and emission of light energy is one of the possible interactions of light with a system. Another interaction can be the inelastic scattering of the light from the system where the energy shift from the inelastic scattering event is equal to a vibrational transition, called a phonon. As in a classical scattering scenario, a larger/heavier object will scatter the incident lighter particle with a small change in the incident energy. In a quantum mechanical system, this process is called Raman scattering as it was initially observed and explained by the Indian physicist Sir Chandrasekhara Venkata Raman using sunlight. A full description requires a proper quantum mechanical derivation, but a simple picture can be constructed using semi-classical ideas. Consider the dipole moment of a system

\[ P = \alpha E \]

where \( P \) is the dipole moment, \( \alpha(\omega_o) \) is the polarizability tensor that oscillates at a unique frequency and \( E \) is the incident electric field. Expanding \( \alpha \) in a Taylor series gives

\[ P = [\alpha_o + \frac{d\alpha}{dQ} \cos(\omega_o t) + \cdots]E \cos(\omega_L) \]

The first term in brackets is the permanent dipole and the second term is the first order expansion term of the polarizability tensor. Trigonometric identities
lead to the expression for the dipole

\[ P = \alpha_0 E \cos(\omega_L t) + \frac{d\alpha}{dQ} \cos(\omega_o t + \omega_L t) + \frac{d\alpha}{dQ} \cos(\omega_o t - \omega_L t) \]

which are the Rayleigh scatter at the incident wavelength \( \omega_L \) and the upshifted and downshifted scattered photons with and energy difference from the incident energy an amount equal to the polarizability oscillation energy. This energy is equal to a vibration of in internal motion of the system. Simple symmetry considerations show that for a system of \( N \) atoms, the degrees of freedom in 3 dimensional space is \( 3N \). There are 3 degrees of freedom for the linear translation of the center of mass and 3 for the rotation of the entire system which leaves \( 3n-6 \) degrees of freedom for internal motion or vibrations. In molecular systems with low symmetry there can be many vibrations. For crystalline systems, or molecular crystals where one can define a unit cell, generally the number \( N \) is small and there will be only a few vibrations available. Considering the vibrations as harmonic oscillators gives a frequency \( \nu \propto \sqrt{\frac{K}{m}} \), so heavier masses will lead to lower energy vibrations. For example C-C and C-O bonds generally lie in the range of 3000\( \text{cm}^{-1} \) (375 meV) and metal-metal bonds lie below 1000\( \text{cm}^{-1} \) (125 meV).

Raman spectroscopy can also provide detailed structural information about the symmetry of a system. Each of the normal modes of vibration can be associated to one of the irreducible symmetry representations of the system. Such symmetry elements are rotations, reflections, and inversions. Details of the use of selection rules is beyond the need here since these materials are in powder form and therefore do not show orientational spectra. However, the ba-
sic process to utilize the selection rules is as follows. Suppose that a particular vibration belongs to an irreducible representation that transforms according to a matrix multiplication $T$ where $T$ is a $3 \times 3$ matrix element acting on the spatial co-ordinates of the atoms. Using polarized light, the electric field of the light can be written as a 3-vector describing the polarization of the incident light. The scattered light’s polarization vector, $S$ will satisfy

$$
\begin{bmatrix}
T_{11} & T_{12} & T_{13} \\
T_{21} & T_{22} & T_{23} \\
T_{31} & T_{32} & T_{33}
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}
= 
\begin{bmatrix}
S_x \\
S_y \\
S_z
\end{bmatrix}
$$

Depending on the elements of the representation matrix $T$, the scattering output polarization components can be, at minimum, determined as binary 0 or 1 depending on the elements of $T$. This high degree of selectivity makes Raman analysis a very simple and powerful tool in spectroscopy. Each vibration could be analyzed with incident and scattering polarization at various angles to determine the symmetry group of each vibration. Raman spectra of the composite materials are discussed in chapter two.

1.7 Ultrafast Spectroscopy

Steady state optical spectroscopy probes the physics of a system using energy, polarization, and the phase properties of light. The time of many quantum mechanical processes happens in the nanosecond or sub nanosecond range. Mechanical or electrical components can provide detector temporal resolution
near the nanosecond range. However in order to generate a time interval on the
order of atomic processes shorter probes of picosecond or femtosecond dura-
tion are needed. With pulses this short, quantum mechanical processes can be
investigated in real time. The basic principle of ultrafast spectroscopy is that
the short optical pulses are probes of the system at time intervals fast enough
to build an time evolving optical signal of the internal processes. Another field
driven by Ultrafast spectroscopy is non-linear spectroscopy using the high peak
powers of short optical pulses to drive non linear effects.

Ultrafast lasers give direct optical views into solid state\cite{8} and biological pro-
cesses \cite{9}. Ultrafast spectroscopy has given detailed information into the pro-
cesses in photosynthesis, carrier dynamics in semiconductors and also allows
novel methods of imaging by using the short time profile of the pulses. The
laser pulses are generated by a broad bandwidth gain medium in an oscillating
cavity and some type of saturable absorber to shorten the pulses. When the
gain medium is externally pumped, usually with another laser, and begins to
oscillate (lase) in the cavity, the saturable absorber will attenuate a portion of
the lasing light until it reaches maximum saturation, and then the remaining
portion of the light now as a temporally shortened pulse transmits through
the saturated absorber. An active system can produce nano-second pulses,
but to easily achieve shorter pulses a passive system is utilized to take ad-
vantage of the faster processes in a molecular system. The ultrafast laser
used for much of this work is a Chameleon laser manufactured by Coher-
ent Inc. It is a Titanium:Sapphire crystal doped with chromium which has
a broad emission in the visible-NIR region of the spectrum. The Ti:Sapph
crystal is pumped with a 532 nm solid state diode laser. With an internal fabry-perot adjustable element, the laser produces tunable pulses from 680 - 1060 nm of 150 femtosecond pulse duration and an average power of 1-4 Watts and a repetition rate of 80 MHz. This gives an average pulse power of 1 Watt / 80 x 10^6 pulses or 12 nanojoule per pulse. The peak power of each pulse is then 12 nj / 150 x 10^{-15} sec = 80 KW peak power. Because of the wide tunability of the Chameleon laser, the output laser is not as sharp as a single line Ti:Sapph laser. Under ideal conditions, the transform limited temporal width of a Gaussian pulse of 150 fs centered at 800 nm satisfies
\[
\Delta \nu \Delta \tau_p = \frac{c}{\lambda^2} \Delta \lambda \Delta \tau_p = \frac{3 \times 10^8}{16 \times 10^{-16}} \times 150 \times 10^{-15} \Delta \lambda = 28.125 \Delta \lambda = 0.44 \text{ or } \Delta \lambda = 1.5 \text{ nm}
\]
The laser bandwidth is closer to 5 nm because of the restriction of the lasing modes transmitted by the internal fabry-perot that allows tunability. An internal spectrometer and diode monitor the wavelength and output power of the laser. In this thesis, ultrafast spectroscopy is used to measure the picosecond decay of the laser induced emission of the composite materials. The 150 fs pulse can be considered a delta function or instantaneous excitation which populates excited states in a region of energy space depending on the incident laser energy. The emission of the material shows signatures of each of the components of the composites, and the ultrafast decay profiles of the emission gives information into the decay channels of the composite materials. Picosecond emission thus gives direct observation of the population of the emissive state, and wavelength selectivity determines the energy levels of the observed emissive state.
1.8 Conversion of Light to Electricity

One of the possible uses for this composite is to generate electrical energy from light, though after study it seems that this compound would be better suited for photo-chemical reactions such as hydrogen production driven by light. Details of cells made from these compounds are given in chapter 5. A photovoltaic cell is a device that converts electromagnetic radiant energy into electrical energy. A solar cell is a photovoltaic that uses sunlight as the input radiant energy. A variety of physical schemes can do this [10, 11], some are biologically alive, some are biologically inspired and others are inorganic solid state systems. Any scheme that accomplishes this conversion will have a few common characteristics. There is a photosensitive region where a photon is absorbed and creates an excited state (electron-hole pair). In order to extract this energy from the excited system there should be some type of spatial asymmetry in the electronic energy landscape that drives the excited electron away from the remaining hole to produce a charge separated state. And finally there should be a donor element to fill the hole of the transiently ionized photo-sensitive element so that the recapture of the excited electron is blocked. Figure 1.8 shows a system based on a triad of elements. The primary photo absorber generates an electron hole pair. The acceptor, which is spatially distinct from the donor, takes the excited electron while the donor passivates the ionized primary which induces a hole in the donor. Usually the donor system is large enough that this hole is stable with respect to the donor energy levels. The charge separated state contains stored potential energy due to the Coulombic energy store in the displaced electrons and holes. If an external circuit connects the acceptor
to the donor, there would then be a down hill energy landscape for the excited electron so that it’s energy can be extracted for external work.

Figure 1.8: The three main components in the model for charge separation in a 3rd generation solar cell. The blue represents the acceptor (a metal oxide), the green split sphere with the yellow electron represents the primary photo absorber (dye or quantum dot) and electron and the red represents the donor system (redox system). The yellow arrow above shows the direction the electron should move to extract energy from the system.

The photovoltaic effect was first observed by Edmond Becquerel, father of Henri Becquerel, in an acidic solution of silver chloride [12]. The development of photography led to much research of activated metals for photographic film using various forms of silver and zinc in later times. These types of photovoltaics are enticing because they are made by solution batch processing, however they usually suffer from low conversion efficiencies due to innate disorder in a molecular system that leads to numerous traps and defects as compared
to long diffusion length and high mobility in long range ordered macroscopic crystalline material. Modern traditional solar cells are made out of crystalline Silicon which has a bandgap of 1.1 eV (1127 nm) in the near infra-red (NIR). Silicon is an homo-nuclear indirect bandgap semiconductor. P-type silicon can be juxtaposed with n-type silicon to create the spatial asymmetry described above and the active region is the depletion region where charge separation takes place. Contrary to crystalline cells, these ZnGO composites are not macroscopically long range ordered, but the crystalline nature and some of the electronic properties of the zinc phase is preserved in the composite form. The metal provides a conduction band for excited electrons, the oxide of the metal provides modification of the energy levels and electron affinity into the metal conduction bands. It can also act as the primary photo-absorber in the system as opposed to photosynthesis which has a dedicated separate photo-absorber system. More on the details of solar cells is discussed in chapter 5.
“And on the sixth day, God said “Let there be light””.

2

Steady State Optical Properties of Zinc oxides and Composites with Graphite Oxide

2.1 Introduction

Zinc Oxide and its various forms are well-known brightly luminescent metal oxides with a fundamental bandgap in the near UV region of the spectrum. The modification of the surface groups leading to Zn(OH)$_2$ and the addition
of Graphite Oxide (GO) shows changes in their spectra consistent with the combinations and interactions of the constituent materials. Tauc plots are calculated from reflectivity measurements and the band gaps determined for the different composites. The emission spectra of the composites are studied with varying excitation and two dimensional plots reveal the evolution of the emission properties with absorption by the Zn phase versus defect emission. The band edge emission of the composites is reduced, and the visible emission intensity and position gives qualitative information of the nature of the defect levels and energy transfer within the composites. With high energy excitations, the exciton emission and the visible defect emission is observed. Excitation dependent spectra of the materials show that there is a large density of defect/gap states that can produce bright emission with excitation energies below the fundamental gap of the Zn phase. The visible emission band of the composite materials becomes that of the defects of neat ZnO under excitation energies below the fundamental gap energy. The blueshifted visible emission is also obtained with high intensity and energies near the band edge at freshly illuminated spots, but quickly (few seconds) decreases and the spectrum returns to the normal steady state emission profile. With sub band edge excitation energies, this blueshifted emission is stable. This implies that these blueshifted emissions are suppressed with a large number of electron hole pairs, possibly due to an electrostatic shift of the fermi-level once quasi steady state conditions are obtained. On the other hand, without direct electron hole generation, there is less of an electrostatic shift due to the excited state manifolds and the states responsible for the blueshifted emission are populated and subsequently
undergo their own recombination events to produce emission. The photophysics of Zn based compounds is a well studied field. Mixtures with other metals and halides have activation properties that were found to have lifetimes ranging from ultrafast to many seconds [13]. The origins of the numerous emission bands are a bit clouded in the effects of defects and adsorbants and absorbants, and also heavily dependent on the surrounding environment and methods of synthesis[14]. The Zinc phase provides a highly polar environment as seen by the Raman intensity of its polar vibrational mode, expected for a metal-oxide. The high electrical affinity of oxygen causes a strong pull on excited electrons as well as centers for traps and potential energy minima of the electrons. These composites of Zinc Oxide and Graphite Oxide have been developed recently [15] via modifications of the ZnO to Zn(OH)$_2$ supporting bonding groups with the highly disordered sheets of Graphite Oxide. Their chemical properties have been studied in depth to understand the specifics of the bonding groups and the role of GO on chemical adsorption and decomposition catalytic activity. Nanoforms of carbon have been intensely studied recently following the discoveries of quantum mechanical electronic effects in graphene and other nano sized old materials. The presence of Carbon in a system defines it to be organic, and so composites with forms of carbon are also a rich testing ground to learn about hybrid systems of organic and inorganic materials. The unique electron bonding configuration of carbon in atomically thin systems leads to strong coupling in the plane of the carbon atoms due to covalent overlap leading to $\sigma$ bonds between carbon atoms. The valence structure leads to a singly occupied state on each carbon atom directed per-
pendicular to the plane of atoms, called the $\pi$ bond which has been found to be able to delocalize over the lattice of carbon atoms. In some systems, the electron mobility of the $\pi$ atoms increases several orders of magnitude. From a chemical standpoint, the presence of carbon supports a wide variety of bonding configurations and the ability to incorporate additional organic materials and structures.

The vibrational and structural characteristics are also compared using Raman Spectroscopy. ZnO is a polar material that shows strong vibrational mode excitation and multi-phonon processes. Inclusion of the GO leads to reduction of the polarity of the composite and reveals a number of defect related modes as well as additional modes unique to the composite material. The Raman signal of GO is usually weak or undetected in the composite materials however it’s presence is shown through the changes in the vibrational modes of the host ZnO / Zn(OH)$_2$ matrix. For most spectra observed, the results were qualitatively reproducible and usually quantitatively reproducible. There are however always observable variations within a simple over time and over different regions of the sample implying a strong interaction with ambient and small inhomogeneity within a sample. In some cases, the luminescence will completely cloud the vibrational spectrum making the Raman analysis a challenge since the defect levels are what cause the irregular macroscopic emission properties.
2.2 Absorption Spectroscopy

Absorption spectroscopy is a basic means of characterizing the electronic energy levels in the system. All of the composite materials were found to be highly insoluble in water or alcohols so that absorption measurements by means of transmission through a cuvette were not possible as the material immediately precipitated. The spectra shown here are for reflectivity measurements done on the powder form of the materials. During the begging of this work, thin films of the material were produced via a hot spray method and the absorption properties determined by transmission were consistent with those of the dry powder, however producing thin films requires large amounts of initial material and so reflection measurements were more appropriate. Also, thin films require high temperature processing which usually led to changes in the material properties either by annealing or by burning. Microscopic regions, or specks within these materials were observed to display strong blue emission that does not coincide with any of the transitions seen in the un-annealed films. The rich blue emission was found to have nanosecond lifetimes and was stable under intense radiation. These isolated blue centers are likely due to the formation of carbon quantum dots or unique ZnO impurity centers. Because of their sparseness and lack of reproducibility to make them, this work does not focus on the rich blue emission.

Figure 2.2 shows the absorption spectra of the composite materials along with GO. The spectra were recorded with an integrating sphere using Halon as a reference and then converted to optical density for subsequent calculations. Common to all the Zinc based materials is a relatively flat absorption
for wavelengths longer than 400 nm implying a lack of strongly resonant electronic energy levels. The absorption is not zero, however for energies below 400 nm. All of the Zinc composite materials show a sharp rise after 400 nm. Graphite Oxide has a broad and featureless absorption profile in the region studied (350 - 800 nm). The dry powder reflectivity has relatively strong absorption > 1 optical density across the spectrum and an apparent inflection point in the absorption curve near 550 nm, in the blue-green region.
The inorganic phase of this composite can be treated as a semiconductor

with a bandedge in the near UV. Although the molecular units of the Zinc phase are small enough that infinite translationally symmetry is not valid, it still preserves much of the features of a semiconductor crystal. The bandedge energy of the material is calculated using the Tauc theory for semiconductor absorption[16]. The derivation here of the absorption edge follows closely the class notes by M. S. Dresslehaus “Solid State Physics II: Optical Properties of Solids”

The absorption of electromagnetic energy by a material is proportional to the rate of transitions from the lower state to a higher energy state. This rate is
calculated using Fermi’s Golden Rule and the rate of transition is

\[ \Gamma \propto \frac{2\pi}{\hbar} \int \langle v|H'|c\rangle \delta(E_c(k) - E_v(k) - \hbar\omega) d^3k \]  \hspace{1cm} (2.1)

\( \Gamma \) is the transition rate, \( v \) and \( c \) are the valence and conduction band wavefunctions, \( H' \) is the perturbing Hamiltonian of the incident radiation. The term in brackets is the matrix element that couples the conduction and valence bands through the light’s Hamiltonian. The delta function term represents conservation of energy of the overall transition in that the energy of the light \( \hbar\omega \) is the difference between the two states. The integral is evaluated over all of \( k \)-space. Simplifying further, the matrix element can be taken as a constant with respect to the wavevector \( k \), then the only remaining term is the integral of the delta function term which is the joint density of states between \( v \) and \( c \). This term that depends on the wavevector \( k \) can be cast into an integral over energy if a form of the bandstructure is known. In general, the joint density of states expressed as a differential in energy space is

\[ \rho_{cv} \propto \int \int \frac{dS}{\nabla_k (E_c - E_v)_{E_c - E_v = \hbar\omega}} \]  \hspace{1cm} (2.2)

The integral is now in energy space, and the surfaces \( S \) are defined as constant energy surfaces with the wavevector \( k \) as the gradient vector. This form shows that there can be strong absorption when two bands are parallel in E-k space. To get any more specific information from this, we need to define some form to the E-k relationship. For a free electrons with an effective mass in each band
the dispersion of the electrons in each band is

\begin{align}
E_c(k) &= \frac{E_g}{2} + \frac{\hbar^2k^2}{2m_c} \\
E_v(k) &= -\frac{E_g}{2} + \frac{\hbar^2k^2}{2m_v}
\end{align}

(2.3) (2.4)

for the conduction electrons and valence electrons and the zero of energy is taken at the center of the band gap. Evaluating the term \(\nabla_k(E_c - E_v)\) gives

\[ \nabla_k(E_c - E_v) = \frac{\hbar^2k}{m_r} \]

(2.5)

defining the reduced mass \(\frac{1}{m_r} = \frac{1}{m_c} + \frac{1}{m_v}\). The joint density of states then becomes

\[ \rho_{cv} \propto \int \int \frac{dS}{\nabla_k(E_c - E_v)} = \int \int \frac{m_r}{\hbar^2k}dS \]

(2.6)

Evaluating this in a spherical geometry where \(dS = 4\pi k^2dK\) gives for the joint density of states

\[ \rho_{cv} \propto \frac{m_r}{\pi^2\hbar^2k} \]

(2.7)

Now for parabolic bands at the gamma point \(\hbar\omega = E_g + \frac{\hbar^2k^2}{2m_r}\) to give

\[ k = \left[ \frac{2m_r}{\hbar^2(\hbar\omega - E_g)} \right]^{1/2} \]

(2.8)

which tells that the joint density of states, and ultimately the absorption coefficient, has the function dependence on the energy as

\[ \rho_{cv} \propto \sqrt{\hbar\omega - E_g} \]

(2.9)
Alternatively, for a transition in an indirect bandgap semiconductor where the transition is accompanied by a phonon absorption/emission process the functional form of the joint density of states becomes

\[ \rho_{cv} \propto (\hbar\omega - E_g + \hbar\omega_q)^2 \] (2.10)

From these equations showing the dependency of the joint density of states on the photon energy, \( \hbar\omega \), we can extract the bandgap energy if we have the absorption spectra. The materials studied in this thesis do not easily form a stable suspension or solution in any liquid so reflectivity measurements were done with the materials in dry powder form. In this case with no transmission, the absorption \( \alpha \) can be approximated with a simplified form of the Kubelka-Monk equation [17]

\[ \alpha \propto h\nu F(R) \] (2.11)

\[ F(R) = \frac{1 - R^2}{2R} \] (2.12)

where \( R \) is the reflectivity of the material. The bandgap energy of the material is calculated using the linear extrapolation to zero absorption of the rising edge of the function \( (h\nu F)^2 \) for direct transitions or \( \sqrt{h\nu F} \) versus the photon energy for an indirect bandgap. The bandgap extracted from the linear extrapolations of the Tauc plots show that there is little variation of the fundamental gap energy with the addition of Graphite Oxide, consistent with other reports of similar composites [18, 19], however there is significant change in the absorption coefficient across the spectrum as well as a greatly broadened
Optical Properties of ZnGO & GO

2.2 Absorption Spectroscopy

Urbach tail into the visible due to the addition of defects and mid gap states. The extrapolations for GO are shown in figure 2.2 for the indirect and direct semiconductor case. Graphene has a completely indirect bandgap in that the energy difference at the Gamma point of the Brillouin zone is a maximum and the bands touch at the edges of the Brillouin zone resulting in a bandgap of zero. Additional layers beyond a single layer of carbon open the gap a small amount, and defects are sure to play a role as well. Considering a direct gap for GO and applying the Tauc formalism gives a value of 2.3 eV which is approximately 540 nm in the green region of the spectrum and corresponds closely to the inflection point of the absorption curve. Interestingly this is almost exactly half the bandgap of diamond which shares a similar carbon carbon bonding network. This also corresponds to the center of the midpoint of the Brillouin zone where the difference between the slopes of the tangent vectors to the dispersion curve changes from increasing to decreasing. Considering an indirect gap for GO and the resulting extrapolation gives a value of 0.45 eV, or 2.75 micrometers. It is possible that the indirect bandgap is responsible for the long extension of the absorption for lower energies. Figure 2.5 is a simplified picture of the energy momentum dispersion of single layer graphene. Although the GO is not graphene, this dispersion is used as a model system. Graphene has been found to be a zero gap material, i.e. the conduction band minimum touches the valence band maximum at a point known as the Dirac point. In graphene, this touching of the conduction and valence bands happens at the edges of the Brillouin zone, while the zone center is the maximal energy gap common to other carbon-carbon bond systems (diamond and long chain poly-
mers have absorptions in the UV region. These high energy UV absorptions are seen in Graphite Oxide, however the striking feature is the strong absorption across the visible spectrum which can not be due to direct transitions between the highest occupied state of the GO molecule to the lowest unoccupied orbital (HOMO-LUMO transition). However long wavelength excitations could be possible for any amount of energy excitation with the simultaneous emission/absorption of a phonon. The small energy photons could be absorbed in a 4 particle process where two photons are absorbed at opposite sides of the Brillouin zone and two associated phonons/vibrations of opposite momentum would be created during the process. Carbon-carbon vibrational quanta are of the order of 200 meV and so very low energy photons could. As the Fermi level reaches closer to the midpoint, lower energy phonons are needed to support a photon transition and less of a momentum change is needed for excitations further from the Γ point. If this were the case, then emission should also be observed into the near infra red which may be observable at low temperatures where the low energy emission is not in the same energy scale of the phonon bath to compete for emission.

In the case of Graphite Oxide, the starting point of the energy level structure would be the simple case above for Graphene, but then allowing a small gap to be induced due to the coupling of the multiple layers and dense defects. Both the direct gap and indirect gap fitting on the absorption dependence show good agreement with the higher energy photon regions and the correspondence to the inflection point supports a “soft” direct gap, in that there is likely a large density of defect states localized in energy space that leads to an inflection in
the absorption curve and a maximum emission for high energy excitation in the red region of the spectrum. Yet also, the fit to an indirect gap properly fits the low energy portion of the absorption spectrum which then means that the GO is also acting as a indirect gap material with vibrational assisted transitions that absorb continuously to lower energies.
Figure 2.3: Tauc plots of the Zinc based materials. The vertical axis is calculated with the Kubelka-Munk equation and the linear fits are drawn by eye and then confirmed with a linear fitting computer algorithm. The last graph shows the calculated value \[ F(h\nu)^2 \] of the materials plotted together on a logarithmic vertical axis.
Figure 2.4: Photoluminescence of commercial ZnO powder, Graphite Oxide, and 2% ZnGO. The excitation was the 325 nm output of a Helium-Cadmium continuous wave laser and detected with a 20 cm spectrometer with CCD detection. Special thanks to Thor Garcia from Professor Tamargo’s lab for use of the instrument.
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Figure 2.5: Tauc plot from reflectivity of Graphite Oxide dry powder for both direct and indirect gap cases. The bottom black curve is for direct gap and extrapolates to a bandgap of 2.28 eV, appx 540 nm. There is still considerable absorptions at lower energies. The upper blue curve is for the indirect gap case which fits better the lower energy portion of the curve and extrapolates to a bandgap of 0.45 eV which corresponds to 2.75 \( \mu \)m light.

\[
\sqrt{hF} \propto (E - E_g - h\nu_{\text{phonon}})
\]

\[
E_g = 0.45 \text{ eV}
\]

\[
(hF)^2 \propto (E - E_g)
\]

\[
E_g = 2.3 \text{ eV}
\]

Figure 2.6: Dispersion of graphene. The vertical arrows are optical transitions and the horizontal black arrow is a phonon transition event. Any energy of excitation would produce an electron hole pair depending on the fermi-level. Graphite Oxide could be considered to have a similar bandgap but with a defect induced splitting at the zone boundaries where the energy levels approach each other. This is calculated to be \( .45 \text{ eV} \).
2.3 Excitation Scans

The absorption edge of the materials does not change with the additional concentration of GO i.e. the fundamental gap absorption is dominated by the Zinc phase. The increase in the amount of GO is observed through the broadband flat absorption and extended Urbach tail of the fundamental gap absorption edge. The broad visible emission band, on the other hand, provides a signature of GO in the composites. Even though the absorption spectra of the composite materials are flat and featureless beyond the main edge, the visible emission varies significantly under excitation of energy below the band gap. Sub-gap excitation creates either strongly bound excitonic states or direct excitation of defect states. These defect absorptions may not be observable with the incoherent and low power lamp used in the absorption scans, but are likely to be populated under intense laser excitation. Even though the Urbach tail does extend farther into the visible range with increasing concentration of GO, the observed absorption spectra does not account for the structures of the observed emissions. For a more detailed look into the energy states of the composite materials, experiments were done with variable laser excitation with energies tunable across the fundamental gap of the system in order to determine the nature of the visible emission and to identify relative energy differences of the states unseen in the absorption spectra.

The optical setup for the excitation scans is shown in 2.3. The fundamental output of the laser tunes between 680 and 1060 nm and then 2nd harmonic generation creates excitations form 340 nm to 530 nm. The lower limit of 695 is used during the experiments because the transmission of the longpass filter
used begins at 345. Quartz optics focus the exciting light onto the sample and a long working distance high numerical aperture microscope objective collects and collimates the light. A longpass filter rejects the incident laser and the light is analyzed by a small Ocean Optics fiber spectrometer. For most of the excitation scans, the fundamental laser was incremented by 5 nm which leads to 2.5 nm steps in the exciting laser wavelengths. However, the tunability of the laser leads to slightly broadened pulses with a center error of 2 nm, so the ultimate resolution is near 5 nm for each exciting laser pulse. The bandgaps extracted from the Tauc plots show the the fundamental gap of the Zn based materials are all near 380 nm, while luminescence is observed for excitations extending to 500 nm. For the following measurements the spectra extend to 450 nm due to signal to noise and integration times.
Figure 2.7: Excitation-emission system. The chameleon laser produces 150 fs pulses tunable between 680 and 1060 nm. The half wave plate and polarizing beam splitter acts as a power tuning unit with a constant output polarization. A 5 cm lens focuses the laser into a BBO crystal to generate the second harmonic frequency. A 15 cm lens is focused onto the BBO to produce a collimated beam with 3x the original spot size. A short pass filter blocks all wavelengths above 680 nm. A 10 cm lens focuses the light onto the sample. At right angle to incident path, an infinity corrected microscope objective, N.A. = 0.4 collects and collimates the light to pass through a longpass filter to remove the incident laser and then into a fiber optic spectrometer. The output power of the fundamental into the BBO is approximately 1 watt and the shortpass filter has approximately 50 percent transmission to give an excitation power of 50 mW.
Figure 2.3 shows the emission of ZnO nanopowder for the series of excitation wavelengths and normalized to the visible emission peak. The near UV emission at 385 does not change position with excitation energy, the apparent redshift is from the transmission edge of the longpass filter which is angled such that the laser does not saturate the detector nor cause an increase in the baseline. It is also important to note that the filters could produce an apparent redshift of the spectrum by reducing the intensity of the high energy edge of the filter, however the filters would not create an apparent blue shift. At high energy excitation there is a broad green emission centered around 520 nm. Similar to the exciton emission this does not change for excitations above the bandedge. A blue emission develops once the excitation energy is lower than the excitonic emission energy and persists until the intensity is too small to be observed.

Figure 2.3 shows the excitation scan of Zn(OH)$_2$ normalized to the value of the visible emission peak near 600 nm. The near UV excitonic emission is unchanged in energy but reduced intensity in this compound. Also noted is that the emission extends to almost 800 nm whereas in ZnO the emission extends only to 650 nm. The overall evolution is similar to ZnO in that a higher energy emission peak dominates for sub bandgap energy excitation. However, in contrast to ZnO, this change does not appear obvious until 20 or 30 nm beyond the fundamental gap. The new peak in the visible corresponds to precisely the same energy as the visible emission seen in ZnO under high energy excitation.

Figures 2.3 and 2.3 show the excitation scans of ZnGO-2% and ZnGO-
20% respectively. Both composites show similar spectral evolution to that of Zn(OH)$_2$ in that the emission spectrum is unchanged through the fundamental gap absorption energy. The spectra also change to the same emission peak as that as ZnO, but for slightly longer wavelengths for the GO composites. The large blue emission of the 20% composite could be due to slight inhomogeneity of the composite which could result in a locally dense area of ZnO, or potentially an effect of weak interaction with the high quantity of surrounding GO.
Figure 2.8: Top: Emission spectra of ZnO nanopowder with excitation from 347.5 to 430 nm incremented by 2.5 nm. Bottom: Same as above but with detail around the emergence of the 450 nm emission. The new peak at 450 nm evolves just after bandedge excitation near 380. The emission is normalized to the value at 520 nm. The oscillations are due to interference effects of the long pass filters.
Figure 2.9: Emission spectra of Zn(OH)$_2$ for excitations 347.5 - 450 nm normalized to the intensity at 575 nm. The appearance of the blue emission at 510 nm occurs below 410 nm which is lower energy than that of ZnO.
Figure 2.10: Emission spectra of ZnGO-2% incremented by 5 nm. The spectra are normalized to the intensity at 575 nm. The blue emission peaked at 510 emerges after 410 nm.
Figure 2.11: Emission spectra of ZnGO-20%. The blue emission peaked at 510 nm emerges sharply after 410 nm excitation. The spectra are normalized to the intensity at 575 nm.
2.4 2D-Excitation Emission Plots

The following images are color contour plots of the above excitation emission spectra. The multi-dimensional nature of these types of plots makes evaluation and analysis more straightforward as the evolutions and broad feature are more easily identified across the image. Additional, the intent is to develop a richer method of spectroscopic analysis that is facilitated by simultaneous multi-dimensional plots. From the following plots it seems likely that the changes in the observed emission spectra occur over continuous transformations, i.e. there is simultaneous emission of the various states for intermediate energies or it may be that the states themselves undergo continuous changes as the energy of excitation moves across the fundamental band edge. Figure 2.4 is the contour plot of the excitation emission of ZnO nanopowder. The main excitonic band is located at 3.2 eV and the visible emission band at 2.4 eV for above gap excitations. The transition in the spectrum occurs precisely at the energy of emission at 3.2 eV. For lower energies the emission is then centered at 2.8 eV, higher in energy than the green visible defect states. The slight redshift of the emission islands is due to the edge of the short pass filter where the laser would dominate the spectrum. Also apparent with the 2D contour plot is the excitation profile of ZnO. There is a local minimum near 370 nm excitation, and two excited states at 360 and 380 nm which agrees well with the absorption spectrum of ZnO. The transformation for Zn(OH)$_2$ and the GO composites are similar among themselves and show strong differences to that of neat ZnO. The 2D excitation scan of Zn(OH)$_2$ is shown in figure 2.4. At 3.2 eV, where ZnO undergoes a change in emission, only a slight increase to
longer energy emission occurs. at 2.9 eV, or approximately 420 nm, the spectrum transforms in a way similar to ZnO in that a new, higher energy emission emerges. However, in the case of Zn(OH)$_2$ and the GO composites, this peak corresponds exactly with that emission seen in ZnO with above gap excitation. No sign of the blue emission at 2.8 eV is seen for these composites.

Research on a similar metal oxide TiO$_2$ found a photo current response that was greater for sub-bandgap excitation. In the case of TiO$_2$ this maxima was found near 420 nm after heat treatment to 500° creates a heavily populated depletion layer near the valence band that couples to the conduction band[20]. Here in the Zn composites the emergent blue peak is around 430 nm. Room temperature $kT$ is approximately 25 meV while this blue emission is almost 300 meV from the excitonic emission of ZnO which suggest this emission is not due to thermal activation or Auger processes from low lying trap states. The close correspondence to the energy as seen in the surface oxygen induced photo activity in TiO$_2$[20]. The bond between a charged oxygen defect and the transition-metal d-orbitals should be similar in energy for those states not immersed in the bulk of the material. Additionally, for these Zn-GO composites specifically, the presence of the hydroxide groups in Zn(OH)$_2$ was found to enhance the photo activity of the parent Zinc compound[21] in comparison to un-modified ZnO. which also confirms the sensitivity of the surface oxygenation on the photon coupling. Figure 2.4 shows the onset of the emergent blue emission versus excitation energy for the series of composite materials. ZnO has the highest energy onset of 3.25 eV just below the excitonic emission energy, to observe the blue emission. The other materials show similar onset energy
near 3 eV, for the onset of the 520 (2.15 eV) which is nearly 1 eV Stoke's shift. Figure 2.4 shows the emission intensity of the blue emission relative to the strength of the longer wavelength visible emission.

From the above spectra, the energy levels of the material can be tentatively assigned. Figure ??levels shows the relative positions of the various materials. The blue emission seen in ZnO is not seen in the GO composites and is a shoulder in Zn(OH)$_2$. The deeper energy levels at 2.1 eV are seen in both Zn(OH)$_2$ and the GO composites. Figure ?? is a schematic of the energy levels in the composite materials. The levels of the ZnO matrix are drawn in a molecular picture and the defect levels are drawn in a molecular/semiconductor picture where the horizontal axis represents the tunneling or transition into the various states.

The diagram shows that multiple emissions are possible. However, it does not immediately explain why the blue emission near 440 nm is not apparent with above gap excitations in ZnO, but becomes dominant for sub gap excitation. The following reasoning gives a possible explanation. The blue emission at 440 nm is from Zinc vacancies in the ZnO matrix. With high energy excitation, the electron hole pair becomes mobile, i.e. the wavefunction can spread through the energy landscape, and the most probably decay route would occur into the lower defect levels. If the hole were to move to outer regions of the ZnO matrix where defects and surface states dominate, then electron hole pair would not be possible at a Zinc vacancy. Now with sub gap excitation, these Zinc vacancies would be directly excited, and the lack of mobility of the electron hole pair would prevent the excitation from tunneling or moving into
other energy minima which is why the lower energy defects are not seen with sub gap excitation.

The Zn(OH)$_2$ emissions weakly exhibits this 440 nm emission, and the composites with GO show no sign of the 440 nm emission with sub gap excitation. This is either a result of the lack of strongly attracting Zn vacancies or stronger delocalization across the energy landscape so that the most probable path would result in a low energy defect state. Zn(OH)$_2$ does show a small change as the energy tunes across the bandgap suggesting a low density or low affinity of these states. In the GO composites, since there is a region of almost 20 nm beyond the bandgap where no change in the emission is observed, it seems that this defect level is reduced in the hydroxide and eliminated or ineffective in the GO composites.
Figure 2.12: 2D excitation emission spectrum of ZnO nanopowder. The lines are labeled by the energies of the intersection on the axes. It is seen here that the transition begins precisely at energies beyond the fundamental gap emission.
Figure 2.13: Excitation emission spectrum of Zn(OH)$_2$. 
Figure 2.14: Excitation emission spectrum of ZnGO 2%.
Figure 2.15: Excitation emission spectrum of ZnGO-20%.
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2.4 2D-Excitation Emission Plots

Figure 2.16: Graph of the intensity relative to the long wavelength visible emission of the blue emission as a function of excitation energy. The bandgap energy is labeled and the decrease to lower energies is due to the transmission edge of the long pass filters.

Figure 2.17: Assignment of energy active energy levels in the various materials. The 2.8 emission is seen as a weak shoulder in the Zn(OH)$_2$ spectrum and absent for the composites with GO.
Figure 2.18: Schematic of the energy landscape showing the main electronic levels of the Zn matrix combined with the molecular defect levels observed in the fluorescence measurements. The vertical arrows represent optical transitions.
2.5 Raman Spectroscopy of ZnGO

Raman scattering spectra provide structural and bonding information of a material and in some cases can give insight into electronic properties under resonant conditions. The Raman scattering spectra of these composite materials were measured to identify signature effects of the inclusion of GO, similar to the emission measurements, in order to focus on details that are unique to the composite nature. ZnO by itself is a highly polar material because of the relatively weakly bound d-orbital electrons of the Zinc and the high electron affinity of the oxygen atoms. The spectra show strong scattering of the main optical phonon modes as well as strong 2-photon processes which confirm the strong electron phonon coupling of the material. The Raman spectra of the composite material show a reduction in the polar nature of the material and small signatures of the GO and additional C-C, C-O, O-O and O-H bonds which confirms the surface modification of the materials relative to ZnO.

The Raman scattering was excited with the two main emission lines of an Argon-Ion laser at 488 and 515.5 nm. The continuous wave (CW) Argon-Ion laser is tuned with a prism at the end of the lasing cavity in the Littrow configuration, i.e. the dispersion of the prism can be matched to the reflection angle for a particular wavelength so that the laser operates in single line operation. A narrow band transmission filter removes any remaining plasma lines from the laser beam and then the laser is directed into a table top microscope. It was found that a microscope objective of 10X produced better spectra than a 100X objective. The signal light was collected in a backscattering geometry and the laser light is suppressed with an edge pass filter specific to the
excitation light. The signal is focused by a 7.5 cm lens onto the entrance slit of a 75 cm single state spectrometer with a nitrogen cooled CCD detector. After a stepwise scan across the emission spectrum, the laser wavelength was changed and the spectrum scanned again. The edge pass filter that suppresses the laser signal transmits beyond 100 cm\(^{-1}\). The samples were somewhat inhomogeneous in that different spots would produce strong fluorescence signals likely from regions of high GO concentration. Not all spots of the composite materials showed the signature Raman lines of GO in the 1300 cm\(^{-1}\) region. Figure ?? is the Raman scattering spectra of ZnO excited with the 488 and 514.5 nm laser lines. Both spectra show the same modes, and the increase in scattering intensity with the 488 nm laser line is attributed to the frequency dependence of scattering which is dependent on the fourth power of the frequency observed. The major optical phonon line at 439 cm\(^{-1}\) has an intensity off the chart shown. The asymmetric feature around 1150 cm\(^{-1}\) can be identified as two phonon processes. Neither the 488 nor 514.5 laser line can directly excite electron hole pairs nor excite into the defect bands of ZnO, therefore little difference is expected between the two spectra.

Figure 2.5 is the Raman spectra of Zn(OH)\(_2\) with the same conditions as above. The major phonon modes from ZnO are still observed in Zn(OH)\(_2\) but with reduced intensity. One additional mode at 863 cm\(^{-1}\) is seen with excitation at 514.5 nm. In the long energy region, not shown here, are additional bands that fall into the region of vibrations between C,H and O which is expected for the modified surface of the Zn(OH)\(_2\) as compared to ZnO The Raman spectra of ZnGO-2% is shown in figure 2.5. The strong polar vibrations of the
ZnO host are reduced in intensity similar to Zn(OH)$_2$ as are the two phonon excitations seen around 1150 cm$^{-1}$. The presence of GO is observed by the G and D bands of graphite but are not shown in these graphs. The baseline of the Raman spectra of ZnGO-2% is significantly enhanced with the 514.5 nm laser line which could be an effect of near resonance of the GO bandedge determined by the Tauc plot in figure 2.2. A series of high energy vibrations are also seen above 2000 cm$^{-1}$ as seen in Zn(OH)$_2$ due to lighter atoms on the surface. Figure 2.5 shows the Raman spectrum of ZnGO-5%. As in the other composite materials, the polar vibrations of the ZnO phase are reduced in intensity. No baseline enhancement is seen with 514.5 nm excitation which is contrary to the assumed effect of GO. The modes at 373 and 385 cm$^{-1}$ do show a slight resonance with the 488 nm excitation. The two phonon lines are observed but of much less intensity than those of ZnO and slightly less than those of ZnGO-2%

These Raman spectra overall agree closely with those reported in the litera-
2 Optical Properties of ZnGO & GO

2.5 Raman Spectroscopy of ZnGO

Figure 2.20: Raman Spectra of ZnO excited with the 488 nm and 515.5 nm laser lines from an argon-ion laser. A baseline is due to defect luminescence and is observed at larger energy shifts. The spectra are normalized to the max value and not offset.

Figure 2.21: Raman Spectra of Zn(OH)$_2$ excited with the 488 nm and 515.5 nm laser.
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2.5 Raman Spectroscopy of ZnGO

Figure 2.22: Raman Spectra of ZnGO2 excited with the 488 nm and 515.5 nm laser lines. The enhanced baseline with the 514 nm excitation is likely due to near resonance of the GO as well as being closer to the visible emission of the composite materials.

Figure 2.23: Raman Spectra of ZnGO5 with 488 nm and 514 nm laser excitation.
Figure 2.24: Comparison of the low energy range Raman Spectra of the composite materials using the 488 nm and 514 nm laser lines.
ture of previous studies of Raman scattering in ZnO and the mode assignments in table 2.1 are taken from the work of Porto[22] and others[23]. The reduction of the main polar vibration at 440 cm$^{-1}$ is reduced in all materials relative to the ZnO nanopowder attributed to the reduced electron attraction of (OH) groups in compared to surface oxygen on ZnO. This modified dielectric environment should change the polar nature of the vibrations. Additionally, the coupling to the GO phase could provide a decay channel for the electrons that would compete with 2 phonon processes which accounts for the reduction in the scattering intensity of the multiphonon processes. Aside from the signature G and D bands of GO in the 1400 cm$^{-1}$ there is no obvious signature of the inclusion of GO, however this is not surprising since the composite material is a heterogeneous mixture of the Zn(OH)$_2$ and GO, and the bonding sites mediating the connecting structure. The fine details below 300 cm$^{-1}$ however do depend on the addition of GO. ZnO nanopowder shows a strong defined mode at 206 cm$^{-1}$, whereas this mode is broadened and then develops into multiple modes with the modification to Zn(OH)$_2$ and addition of GO. We can attribute these to defect related states, or local vibrational modes, [24, 25] which further confirms the small deformations of the Zn phase by its bonding with GO sheets. The higher energy modes fall into the region of lighter mass vibrations. The vibrations are a combination of oxygen, OH, and carbon bonds as well as bonding between Zn defects (interstitials and vacancies) with atmospheric oxygen creating shallow defect levels??. The collection of Raman spectra of these materials show that the polar nature of the ZnO phase is reduced upon modification to Zn(OH)$_2$ but the energy levels of the vibrational
modes are unchanged which confirms the persistent of the atomic arrangement of the host phases. Higher energy vibrations unique to the modified composites show that there are a number of surface/defect related vibrations that originate from the (OH) groups on the ZnO and GO sheets together. Finally, the low energy spectra show details of the nature of the defects incorporated with the addition of GO. Table 2.1 tabulates the observed Raman signals and their assignments.

Figure 2.25: Higher energy vibrational modes of the composite materials excited with 488 nm laser. Peak positions are labeled in each case. The multitude of vibrations above 2000 cm$^{-1}$ are moderately consistent.
### Table 2.1: Raman mode energies (cm⁻¹) observed of the parent and composite materials

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<th>Zn(OH)₂</th>
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<td>206</td>
<td>206</td>
<td>211</td>
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<td>Defect induced</td>
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<td></td>
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<td>332</td>
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<td>333</td>
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<td>384</td>
<td>373</td>
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<tr>
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<td>412</td>
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"Light is like a woman, you’ll never understand it and it will never do what you want" - Dr. J. D. Garcia

3

Time Resolved Emission of ZnGO

Parts of this chapter are published in the Journal of Photonics for Energy under the title “Time Resolved Fluorescence and Ultrafast Energy Transfer in a Zinc (hydr)Oxide-Graphite Oxide Mesoporous Composite” J. Photon. Energy. 5(1), 053084 (Dec 10, 2015). doi:10.1117/1.JPE.5.053084
3.1 Abstract

Ultrafast energy transfer from a zinc (hydr)oxide unit to a graphite oxide phase in a hybrid organic/inorganic composite is studied via time resolved fluorescence spectroscopy. The time resolved emission is spectrally decomposed into emissions originating from the zinc (hydr)oxide optical gap, zinc (hydr)oxide surface trap states, and the graphite oxide. The radiative lifetime of graphite oxide in the composite becomes an order of magnitude longer than that of graphite oxide alone while the radiative lifetime of the zinc optical gap is shortened in the composite. An energy transfer scheme from the zinc (hydr)oxide to graphite oxide is considered.

3.2 Introduction

Utilizing the energy from solar radiation is at the forefront of current research. Generating electrical energy from solar photons requires strong absorption and subsequent generation of a long lived electron hole pair to either generate an electrical current or an excited electronic state to drive a chemical reaction. In contrast to fabrication intensive crystalline photovoltaic systems, molecular metal oxides are being studied as an alternative approach to solar energy harvesting. Generically known as Grätzel Cells [10], the photovoltaic system consists of a large bandgap metal oxide (i.e. ZnO or TiO₂) and a smaller bandgap sensitizing element for an enhanced spectral range of light collection. A challenge in these materials is to maintain the photogenerated exciton against recombination mechanisms present in the molecular system [26]. One
approach to overcome this challenge is the addition of an organic carbon phase acting as an electron acceptor/sink with long lived excited states in addition to enhanced conductivity for charge extraction. These composites have been used in solar cell devices in a Grätzel cell configuration[27], and also have shown enhanced conductivity with the inclusion of graphite oxide[28]. In this study, the optical properties and time resolved emission of the hybrid organic/inorganic composite of zinc (hydr)oxide and different amounts of graphite oxide (ZnGO2 and ZnGO5 where 2 and 5 are weight % of graphite oxide) are used to study the energy landscape within the metal oxide–graphite oxide composite. The radiative lifetime of the graphite oxide (GO) is found to increase several fold when in the presence of the zinc (hydr)oxide along with a reduction of the radiative lifetime of the zinc (hydr)oxide phase signifying an efficient energy transfer system.

3.3 Experimental Methods

Synthesis and chemical analysis of the ZnGO composites have been thoroughly investigated by the Bandosz chemistry group[1, 3]. Briefly, GO was synthesized by oxidation of graphite (Sigma-Aldrich) using the Hummers method. The composites were prepared by dispersing GO powder (2wt.%) of the final mass of the material in 1.0 L zinc chloride solution (0.05 M). The resulting well-dispersed suspension was stirred for 4 hours. Sodium hydroxide solution (0.05 M) was then added (2.0 L) with a rate of 2.0 mL min-1 using a Titronic Universal (SCHOTT) method. Afterwards, the obtained composites were extensively washed with distilled water until neutral pH and no traces of chloride
Figure 3.1: (top) SEM image of the ZnGO2 composite. The scale bar is 10 microns. (bottom left) Absorption spectra of ZnO (black), ZnGO2 (blue), ZnGO5 (dark blue), and GO (red). Absorption spectra were recorded from reflectivity in an integrating sphere. (bottom right) Emission spectra of ZnO (black), ZnGO2 (blue), and GO (red). Emission spectra were done with 325 nm excitation from a HeCd laser and the signal collected by a 25 cm spectrometer and CCD detection. The irregularities around 700 nm in the emission spectra are due to spectrometer optics. Overlaid on the plot of emission curves is the absorption curve again of GO (thin red). All spectra were done with the material in dry powder form under ambient conditions.

ions were found. Finally, the suspension was centrifuged and a gel formed was dried at 100°C over 48 hours. Zinc (hydr)oxide was prepared in the same way, without the GO in ZnCl2 solution. The top of Fig.3.1 is a scanning elec-
tron microscope (SEM) image of the ZnGO2 composite showing a mesoporous structure with a large surface to volume ratio the the composite structure as a web-like network. The bottom of Fig.3.1 shows the absorption ZnO, ZnGO2, ZnGO5 and GO. GO is a black powder, and the absorption spectra is relatively structureless with strong absorption across the 350-800 nm range. The composite materials show a similar absorption edge of the ZnO optical gap, an enhanced absorption baseline proportional to the amount of GO. The emission spectra (bottom right) show the emissions under 325 nm HeCd laser excitation. The absorption spectra of GO is overlayed on the emission spectra to show the spectral overlap of the ZnO emission and the GO absorption. All optical spectra were done with the dry powder of the materials lightly pressed under a 0.5 mm quartz cover plate. The ZnGO composites fluoresce yellow-red similar to GO by itself, while the ZnO glows white due to the strong emission in the blue region of the spectrum. The blue emission between 400 and 500 nm seen in other reports of GO[29] is observed as a small shoulder in our neat form of GO suggesting a small amount of reduced GO, however the dominant emission is in the red region of the spectrum. Lastly, we note that the broadband visible emission of the composite materials centered at 520 nm shows the same onset characteristics at 500 nm as that of the emission of GO.

The steady state of the composites have a greatly reduced emission in the blue region associated with the zinc (hydr)oxide optical gap which could indicate efficient quenching of the zinc (hydr)oxide by the GO. Strong resonant energy transfer is possible with cases with small amounts of GO functionalized to the nano-materials; additionally GO is able to effectively quench the excited state
of nanomaterials and dyes because of the large density of states afforded by GO defects which are energetically positioned favorably with regards to metal nanosystems\[30, 31, 32\].

### 3.4 Streak Camera Operation

The streak camera measures luminescent events in the time domain with a lower time limit resolution of 20 picoseconds. The basis of the operation is similar to a cathode ray tube television. A schematic of the streak camera is shown in figure 3.2. The incident pulsed signal of photons is focused onto a photo-cathode that ejects electrons. The ejected electrons carry the same temporal profile as the incident photon pulse. Next a time dependent electric field deflects the electrons a they pass through the streak area. This electric
field is synchronized by an external trigger diode so that subsequent signals can be averaged with consistent timing. The time dependent electric field causes the pulse of electrons to be spread in the transverse direction which then translates the temporal profile along the initial propagation direction into a spatial spread of electrons in the transverse direction. These electrons impinge upon a phosphor screen which is imaged onto a camera giving intensity versus position, the position axis now scaled to the temporal axis by the action of the internal electric field on the electrons. Calibration of the time axis is done with a partially reflective optical resonator cavity, called an etalon. Details of the etalon signal is shown in fig 3.3. The etalon consists of a two partially reflective and partially transparent windows to create a resonator cavity to produce a pulse train with a time separation between pulses equal to twice the optical path length between the partially reflective surfaces. In the etalon used for the streak camera calibration, each surface has a transmission of approximately 10% and the separation between the reflective surfaces is 100 picoseconds round trip. With careful alignment of the etalon, hundreds of pulses can be generated this way. The resulting signal on the streak camera is a series of pulses separated in time by twice the cavity length and with diminishing intensity according to the reflectivity and transmission of the cavity surfaces. Shown in the figure is the response for the slowest time setting of the streak camera with a window of 1200 ns. Faster time ranges give enhanced resolution. As a check on the operation of the streak camera, erythrosin B is used as a test sample. Erythrosin is a brightly emitting dye that is very sensitive to the polar environment of the solvent. The radiative lifetime in water is 89 ps.
Figure 3.3: Ray trace of a pulse passing through an etalon to demonstrate temporal calibration of the streak camera. The angle of incidence into the etalon ideally zero to make the subsequent pulses arrive at time intervals of $2L/c$. The angle is exaggerated in the figure for clarity.

Figure 3.4: The recorded streak camera signal from the etalon for calibration of the streak camera. The linearity in the time axis shows a constant difference between pulses and the intensity axis is approximately linear. Each subsequent pulse has been reflected twice and transmitted once, so the intensity drops by $R^2 \times T$. The later times beyond 500 ps do not show the correct intensity decay which is problematic when fitting slowly decaying signals. A sweep voltage output is monitored by oscilloscope and shows no irregularities of the sweep signal.
Figure 3.5: Streak camera measurement of erythrosin dye in methanol and in water. Each graph shows the trace for the four different time ranges of the streak camera showing good consistency across the time ranges. The graphs were shifted in the horizontal to match the peak intensity and normalized.
(REF TABLE OF DIES) and becomes brightly luminescent in water with a radiative lifetime of 470 ps in methanol in very good agreement with these measurements.
3.5 Time Resolved Emission of ZnGO

To better understand the energy transfer kinetics between the zinc (hydr)oxide to the GO we use time resolved fluorescence spectroscopy (TRF) to measure the kinetics of the emissive states of the composite. The TRF is generated with a 10 picosecond pulse of a diode pumped YAG laser externally doubled to the 4th harmonic at 266 nm. The 4th harmonic light is isolated from the 532 nm light by two UV short pass filters and focused onto the sample with quartz optics, while the collection optics do not transmit the 266 nm excitation.

Figure 3.6: Picosecond transient fluorescence spectroscopy system. The laser source is a Nd:YAG laser emitting 12 ps pulses 82 MHz repetition. The 1064 nm emission is internally doubled in the laser cavity and the 532 nm output was used. A small portion of the pulse is split off by a quartz beam splitter (BS) and sent to a trigger photodiode that resonates near 82MHz and sends the synchronization signal to the streak camera. An electrical delay box can add additional delay if needed. The 532 pulse is then focused with a 10 cm lens into a KDP crystal in a precision mount to generate the harmonic of 266 nm. Two ultraviolet narrow band filters (NBF) remove the 532 nm light. Two 20 cm focal length quartz lenses refocus the 266 nm light onto the sample. A set of back to back infinity corrected long working distance objectives (N.A. = 0.4) collect the signal light and images it onto the entrance slit of the streak camera. Narrow band filters (NBF) or long pass filters were placed in the path of the collimated light between the objectives to remove UV excitation from the signal. Although no 266 nm UV light was seen to be transmitted through the objectives.

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Figure 3.7: Time resolved emission decay curves of ZnGO2, ZnGO5, GO and ZnO nano powder. The emission curves of ZnGO2 and ZnGO5 are labeled according to the narrow band filters used for the measurement: 400 nm ± 20 nm, 510 nm ± 10 nm, and 670 nm ±10 nm. The solid lines over the data symbols are the exponential fits discussed in the text.

A small portion of the 532 nm pulse is sent to a trigger diode for synchronization of a streak camera. The power of the 266 nm light was kept low enough such that changes in the incident power did not change the kinetic trace characteristics. Measured time resolved fluorescence curves are shown in fig.3.7. The decay curve for neat GO is measured without spectral filtering since the kinetics of the neat GO were not dependent on detection wavelength. The ZnO emission curve was also measured without spectral filtering since the ZnO nano powder exhibits a flat, but non-zero emission for wavelengths longer...
than 500 nm (data not shown).

Figure 3.8: Energy decay/transfer pathways from Zn into GO with the rates considered in the model. Populations are given as $n_i$ and rates between states are $k_{ij}$. The observed signals are from $k_1$ (400 nm), $k_{20}$ (510 nm) and $k_{34}$ (670 nm).

Time resolved emission measurements are useful to characterize the energy states of the molecular energy transfer processes in a material[33, 34] by identifying population kinetics of the emissive states. Figure 3.8 is a proposed energy level scheme of the energy transfer pathways within the composite. For a pulsed excitation, the population change of a state $n_i$ is given by \( \frac{dn_i}{dt} = \sum k_{ij}n_j \) where the diagonal terms $k_{ii}$ are comprised of the sum of all transitions out of state $i$ and off diagonal terms $k_{ij}$ are filling of state $j$ from state $i$. For the
model show in fig.3.8 this leads to the set of equations:

\[
\begin{align*}
\frac{dn_0}{dt} &= -k_0n_o \\
\frac{dn_1}{dt} &= k_0n_o - (k_1 + k_{12})n_1 \\
\frac{dn_2}{dt} &= k_{12}n_1 - (k_{20} + k_{23})n_2 \\
\frac{dn_3}{dt} &= k_{23}n_2 - k_{34}n_3
\end{align*}
\]

This can be cast into a matrix eigenvalue equation with a rate matrix \( R \) acting on the population state vector \( \vec{N} \)

\[
\frac{d\vec{N}}{dt} = R\vec{N}
\]

\[
\begin{bmatrix}
\frac{dn_0}{dt} \\
\frac{dn_1}{dt} \\
\frac{dn_2}{dt} \\
\frac{dn_3}{dt}
\end{bmatrix} =
\begin{bmatrix}
-k_* & 0 & 0 & 0 \\
0 & k_* & J & 0 \\
0 & 0 & k_{12} & F \\
0 & 0 & k_{23} & -k_{34}
\end{bmatrix}
\begin{bmatrix}
n_0 \\
n_1 \\
n_2 \\
n_3
\end{bmatrix}
\]

With \( J = -(k_{10} + k_{12}) \) and \( F = -(k_{20} + k_{23}) \). Because this is upper diagonal, the secular equation leads to the set of eigenvalues consisting of the diagonal entries \( \{\lambda\} = \{-k_*, J, F, -k_{34}\} \). The assumed condition that leads to this simple solution is that there are no uphill or backwards transfers and also that there are no transfer rates from the Zinc directly to the GO which would give a \( k_{13} \) term in the upper right. The time dependent population vector is found by solving for the eigenvectors and writing down the populations as
\[ n_i(t) = V_{ij} C_i e^{\lambda_i t} \]

with \( V_{ij} \) the matrix of eigenvectors and the \( C_i \) are constants that can be solved with the initial conditions. Assuming a delta function excitation of state \( n_0 \) this can be solved analytically to give the solutions

\[
\begin{bmatrix}
  n_0 \\
  n_1 \\
  n_2 \\
  n_3
\end{bmatrix} =
\begin{bmatrix}
  N_0 e^{-k_* t} \\
  \frac{k_* N_0}{J + k_*} (e^{J t} - e^{-k_* t}) \\
  \frac{k_* k_{12} N_0}{(J + k_*) (F + k_*) (F - J)} ((J + k_*) e^{F t} - (F + k_*) e^{J t} + (F - J) e^{-k_* t}) \\
  \frac{k_* k_{12} k_{23} N_0}{(J + k_*) (F + k_*) (F - J)} (\alpha e^{F t} - \beta e^{J t} + \gamma e^{-k_* t} - (\alpha + \beta + \gamma) e^{-k_{34} t})
\end{bmatrix}
\]

with \( \alpha = \frac{J + k_*}{F + k_{34}}, \beta = \frac{F + k_*}{J + k_{34}}, \gamma = \frac{F - J}{k_{34} - k_*} \) are multiplying ratios depending on the difference between decay rates between the states.

The resulting decay rates found with this model show that there is a similar fast component to the intermediate 510 nm emission from the composite of approximately 50 ps. In the 5\% sample the amplitude of this fast component is reduced significantly compared to the 2\% composite. We attribute this then to the decay back into the zinc phase of the composite. Accordingly the longer lifetime of the 510 nm emission carries a stronger amplitude of the decay as
there is more GO available causing a stronger decay into the GO. The deep red emissions are found to be similar for both composite which then suggests the low energy emissive states are mostly associated with the GO phase by itself. But as compared to the neat form of GO the lifetime is an order of magnitude larger in the composite. This could come from multiple sources; filling from the zinc phase, reduction of the defects of GO because of bonding to the zinc phase as well as a modified electronic environment unique to the composite material. The details of this mechanism are currently being studied with excitation energy dependent experiments. While intense photo-excitation can chemically reduce GO resulting in a change of spectral properties [29], these ZnGO composites show no permanent spectral changes in their emission after irradiation, which could be indicative of a redox transfer, therefore we consider the decay to be a measure of energy transfer within the molecular composite instead of irreversible photo-chemical reduction of the GO. Efficient energy transfer into the Graphite Oxide is made possible by a broad distribution of the defect energy levels in the energy space of GO, even though the main absorption of GO is at a higher energy[35] than the zinc (hydr)oxide surface states. Excitation-emission measurements of GO have shown that emission can be produced with excitation energies much lower energy than the main ultra violet absorption bands of GO through localized vacancies and attached functional groups within the honeycomb carbon network GO[35] Therefore the excited surface states of the zinc (hydr)oxide are likely to have large overlap (see fig.3.1) with the range of defects levels of the GO that would lead to a hybridization of the interface states facilitated by the short distance separation
of the chemical bond between the zinc (hydr)oxide and the GO[1].

The steady state of the composites have a greatly reduced emission in the blue region associated with the zinc (hydr)oxide optical gap which could indicate efficient coupling of the zinc (hydr)oxide to the GO. In contrast to a donor-acceptor pair, we consider this a composite molecule rather that functionalization of the Zinc phase by the GO. Since the atomic mass of carbon is much less than zinc, 2% weight of GO leads to roughly one carbon atom for every 10 zinc atoms. As seen in the SEM image of 3.1 the ZnGO material has homogeneous morphology versus isolated regions of the Zinc phase with attached units of GO. The visible emission of the composites emits a similar color to that of neat GO, the spectral shape and energy onset of the composite material is also more similar that of neat GO. The visible emission from ZnO by itself has been studied in depth and originates from defect and surface trap state emission[36]. Our measured values of the radiative lifetimes of ZnO agree well with previous reports of sub nanosecond lifetimes, in part due to the increased surface area leading to a large ratio of surface trap states to optical gap states[37, 38, 39]. Because the Zn(OH)$_2$-GO composite visible emission is much more that of the red GO emission, the specific nature of ZnO nano crystal surface states is not apparent in the spectral properties of the composite. Previous reports of steady state spectroscopy have found various forms of GO to effectively quench nanomaterials and dyes.[30, 31, 32, 40]. To better understand the kinetics of this composite, ultrafast TRF is useful to characterize the energy states and molecular energy transfer processes in a material[33, 34] by identifying population kinetics of the emissive states. The blue emission of
ZnO shows a bi-exponential decay with a fast component of 38 ps and longer time constant of 225 ps. Blue emission of the ZnGO2 and ZnGO5 composites have a shortened lifetime relative to the blue emission of the neat ZnO powder. The blue emission of ZnGO5 shows a even faster decay lifetime than ZnGO2 though both are near the 20 ps resolution of the detection system. Thus we conclude that the ultrafast decay processes of the Zn phase composite are faster than that of pure ZnO. The decay of green emission measured at 510 nm is not observed in either the neat ZnO or GO. Although the ZnO has a strong steady state emission at 510 nm, the long decay is not observed in a 400 ps window of the streak camera. Its effect is seen as a small offset at zero time which is removed in the fit of the decay curve. The 510 nm emission of the composite material however is clearly observed in our time window. Since GO shows trivial decay signal in the 510 nm window we conclude that the 510 nm decay is unique to the composite material. Finally, the long wavelength, low energy decay becomes longer compared to the neat GO. The powder form of GO has a dominant decay of less than 20 ps and a smaller lifetime component of 73 ps which is in agreement with other works [41, 42] of ultrafast decay of GO. These fast decay are attributed to the numerous chemical functional groups and lattice defects present in GO network. In composite form, the deep red emission shows single exponential decay of approximately half a nanosecond. This is also evidenced by the moderate offset at zero time due to the long lifetime of the emission still present 12 ns later when the next pulse arrives.

Intense photo-excitation can chemically reduce GO in solution resulting in a change of spectral properties [29]. However, in the case here the ZnGO com-
posites show no permanent spectral changes in their emission after irradiation, which would be indicative of a redox transfer, so we conclude that the energy is transfered from the zinc (hydr)oxide to the GO instead of photo-chemical reduction of the GO. Efficient energy transfer into the Graphite Oxide is made possible by a broad distribution of these defect energy levels in the energy space of GO, even though the main absorption of GO is at a higher energy[35] than the zinc (hydr)oxide surface states. Excitation-emission measurements of GO have shown that emission can be produced with excitation energies much lower energy than the main ultra violet absorption bands of GO through localized defect states on GO[35] Therefore the excited state energy of the zinc (hydr)oxide surface state is likely to be resonant with a defect level of the GO, and the energy transfer is further facilitated by the short distance separation of the chemical bond between the zinc (hydr)oxide and the GO[1].

Table 3.1: Measured Radiative Lifetimes in picoseconds of the three spectral regions. Two lifetimes and the relative fitting weight are given for the signals with biexponential fits. Where no signal or decay is observed the entry is n/a. Upper/lower bounds are estimated for lifetimes beyond the limit of resolution of the streak camera.

<table>
<thead>
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<th>Material</th>
<th>380 nm τ</th>
<th>380 nm %</th>
<th>510 nm τ</th>
<th>510 nm %</th>
<th>670 nm τ</th>
<th>670 nm %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>38</td>
<td>37</td>
<td>&gt;1000</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>GO</td>
<td>n/a</td>
<td>n/a</td>
<td>15</td>
<td>85</td>
<td>73</td>
<td>15</td>
</tr>
<tr>
<td>ZnGO-2%</td>
<td>&lt;20</td>
<td>46</td>
<td>20</td>
<td>429</td>
<td>405</td>
<td></td>
</tr>
<tr>
<td>ZnGO-5%</td>
<td>&lt;15</td>
<td>48</td>
<td>5</td>
<td>405</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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3.6 Conclusion

In conclusion, the steady state and time resolved emission from a mesoporous carbonaceous/inorganic composite of Zn (hydr)oxide-Graphite Oxide were measured. The spectral overlap of the constituents, reduction in lifetime of the Zn unit emission, and extension of emission from the GO phase suggest an efficient energy transfer pathway from the Zn (hydr)oxide into the GO possibly mediated by hybridization of the zinc (hydr)oxide and GO surface states. No irreversible laser induced reduction of the GO is observed which suggests this to be an efficient energy transfer system which would be beneficial for photovoltaic and photocatalytic processes. It should be noted that excitation with 266 nm can directly excite both the Zn and GO phases of the composites. However, the small fraction of GO by weight should lead to a signal dominated by absorption by the Zn based phase. Further experiments with lower energy excitations are discussed in the next chapter.
4.1 Introduction

The aim is to measure and analyze the energy landscape in the ZnGO composite materials in order to determine the multitude of energy states, the effect of the defect states on the photophysics and the effect of the GO. Both ZnO and
Zn(OH)$_2$ show complex steady state emissions from transitions between the Zinc phase near UV resonances well as broadband visible emission originating from surface states, defects and vacancies. The emission spectrum of graphite oxide also shows a broadband visible emission, further to the red than the visible emission from the zinc based materials. The bandgap of GO extracted from the Tauc plots is near 2.25 electron volts in the green region of the spectrum when considering a direct gap system, or is near 500 meV if considered as an indirect gap system. In the latter case, vibrational modes would strongly couple to the electronic levels. This emission is unchanged for different excitations unlike the Zn based materials, however, similar to the Zn materials the broad emission has its origins in defect states and adsorbants within the GO planar network. Carbon vacancies, epoxide and oxide functional groups, and other local defects lead to numerous defect states which can cause electron hole recombination to energy levels within the band gap of the GO. This then begs the question as to how the broad distribution of defect states of the two systems, the Zn and GO, could interact when in the composite form.

Surface states are by their nature localized near the surface of the system and often have a small wavefunction spread because they originate from site defects instead of topological, long range order or degeneracy delocalized across a system. However, being tightly bound to the surface does not a priori minimize their interaction with the other phase since the surface to volume ratio is significantly enhanced in nanoscale systems, and the molecular composite has chemical bonds between the Zn phase and the GO. Additionally, the native form of the GO is layered sheets which would also contribute a large num-
ber of surface and defect states in the GO. Finally, SEM imagine provided by Mykola Seredych and others in the Bandosz group show that the material is homogeneous in that the zinc phase is nowhere distinct from the GO phase, again suggesting this is not a case of functionalization but rather a new system distinct from each of the constituent phases. Therefore we consider the possibility of hybridization of the surface states of each phase leading to shared surface states of the two phases. The optical gap properties of the zinc phase are moderately preserved as are the spectral features of the low energy GO emission, although their lifetimes are considerably changed when in composite form. The intermediate emission seems to share no feature of either phase and here we study in detail the spectroscopic properties of the composite and the energy kinetics that are unique to the composite phase.

The hypothesis is that signatures of the intermediate electronic states that mediate the energy transfer can be distinguished by observing the emission kinetics with variable excitation energy. For energies above the fundamental gap of the Zn, a cascading process of the energy ensues that includes the Zn UV emission, its own trap state emissions and the emissions of the GO like defect states. Resonant excitation of the Zn phase should lead to a marked increase in the charge transfer state if this is coupled to the electron hole pair of the Zn phase. For energies below the fundamental gap of the Zn, only those excitations into the defect levels should be observed and their role in the transfer/hybridization can be observed.
4.2 Experimental System

The optical layout for the experimental system is shown in figure ???. The light source for the measurements is a chameleon laser that outputs 150 femtosecond pulses that are tunable between 680 and 1060 nm. A half waveplate paired with a polarizing beam splitter act as a neutral density filter to maintain the output power at approximately 1 W. A portion of the fundamental wavelength is split off to trigger the streak camera and the main portion of the pulse is focused into a BBO crystal for harmonic generation of short wavelength pulses. The BBO is placed on a rotation mount in order to obtain 2nd harmonic generation phase matching conditions across the tuning range of laser. The BBO is placed on a translation stage to compensate the change in position of the crystal due to the off axis rotation mount. A short pass filter with a cutoff at 685 nm is placed in the collimated output of the BBO to remove the fundamental laser in the NIR. Next, a 15 cm quartz lens focuses the 2nd harmonic onto the sample which is placed at an angle of approximately 30 degrees so that the specularly reflected beam does not pass into the collection path to the detectors. A long working distance microscope objective with NA = 0.4, magnification 50X, collects and collimates the luminescent signal. This collimated beam is passed through a mechanically tunable narrow band filter (\(\Delta \lambda = 20nm\) bandwidth) for spectral decomposition of the luminescent signal. A flip mirror is able to monitor the signal that is sent to the streak camera. A final longpass filter is employed to suppress any residual excitation light scattered from the sample. To achieve polarization discrimination a Wollaston prism placed on the aperture of the focusing objective splits the signal into complimentary polarization
components. The two beams are sent into the back aperture of a second long working distance microscope objective (NA = 0.4, magnification 20X) and the small divergence angle from the Wollaston prism produces two separated spots in the image plane of the second microscope objective, which is the entrance slit of the streak camera. The entrance slit of the streak camera was kept less than 50 microns with good signal collection intensity afforded by the small spot size generated by the microscope objectives. Samples in dry powder form were placed in a custom sample holder with a 0.5 mm quartz cover disc. Tunability of the fundamental laser is provided by an adjustable Fabry-Perot cavity inside the laser head, though this is proprietary information of Spectra-physics. The time delay of the signal onset was seen to increase with increasing wavelength of the chameleon which causes a constant offset in the luminescence decay that can easily be accounted for. Beyond 900 nm of the fundamental, the photodiode trigger of the streak camera becomes irregularly responsive. The luminescent decay traces were collected as the average of 100 scans of 0.5 seconds each making a total of 50 seconds per integration. The background was collected immediately afterwards with the exciting laser blocked in front of the sample and the aperture open to the streak camera in order to remove any ambient signals captured during integration. After each collection, the flip mirror was inserted so that the next bandwidth position of the tunable filter could be set by observing the signal recorded by the Ocean Optics spectrometer. The purpose of the flip mirror in this case is to maintain reproducibility of the wavelength region scanned for different measurements. Gain settings of the streak camera were kept constant for each excitation wavelength used in
order to maintain a consistent baseline. All of the samples shown below exhibited constant luminescence during the course of the experiment, i.e. no sample photo-degradation was observed as a result of constant laser irradiation. For each excitation, up to 9 scans were taken starting at 400 nm emission and incrementing by $\Delta \lambda = 40$ nm to 720 nm. The exciting laser was incremented by 20 nm of the fundamental which steps the exciting light’s wavelength by
4 Spectrally Resolved Ultrafast Emissions of ZnGO

4.2 Experimental System

Figure 4.2: Four representative raw data traces showing the time decay of the luminescent signal. The streak on the right is parallel to the incident polarization and the streak on the left is perpendicular. These are streak images of ZnGO2 excited at 347.5 nm and the emissions are 400 nm, 480 nm (top right), 600 nm (bottom left), and 680 nm.

$\Delta \lambda = 10\text{ nm}$. Most materials show luminescence with sufficient signal to noise up to an excitation of 420 nm which makes 7 different excitations scans for each material or a total of 63 images for each material. With polarization discrimination a total of approximately 100 decay traces are recorded for each material. Batch processes and automation would be extremely useful for faster
and more reliable experiments. At the moment, the chameleon laser can be easily incorporated into an automated system. However, the streak camera frame grabber computer card is not obviously compatible with any external communication system since the connected computer has no communication ports.

4.3 Results

4.3.1 Zn(OH)$_2$

![Figure 4.3: The two distinct emission profiles of ZnOH$_2$ found with high (347 nm) and low energy (430 nm) excitations.](image)

Spectrally resolved scans for Zn(OH)$_2$ and ZnGO-2% are presented in this chapter. First is presented the results of Zn(OH)$_2$. There are two distinct emission profiles of Zn(OH)$_2$ as discussed in chapter 2. These two distinct
emission spectra are shown again here for reference. With sub band gap energy excitation, the peak of the emission blueshifts to approximately 520 nm and the longer wavelength emission decreases to become a shoulder in the emission spectrum. Figure 4.4 is a three dimensional representation of the time resolved emission. The horizontal axes are time in picoseconds, the vertical axis of each plot is the excitation wavelength, and each graph corresponds to a narrow band region of the emission spectrum. In this way each emission region is analyzed based on the energy of excitation. Each curve is normalized to the maximum value for comparison across different emission and excitation wavelengths. The band edge emission around 400 nm is ultrafast (~30 ps) for all excitations that give rise to the exciton emission. Weak tails are seen that match the excitation profile of the material at 350 and 380 nm excitation. As the emission band wavelength increases towards the low end of the spectrum, the time different emission regions show similar decay trends that also mimic the excitation spectrum of the material. In all emission bands, a longer lifetime is seen for excitations beyond the band edge of 380 nm. Also, for an excitation of approximately 415 nm, the decay becomes longer. This effect becomes more pronounced in the lower energy region of the emission. This suggests that there is an additional, yet undetected state at 415 nm that couples strongly to low energy emissive states.
Figure 4.4: Time resolved emission traces of Zn(OH)$_2$ for different narrow band regions. The vertical axis of each plot is the excitation wavelength and the narrow band emission region is labeled for each graph. Each curve is normalized to the maximum value.
4.3 Results

4.3.2 ZnGO-2%

Figure 4.5: The two distinct emission regimes of ZnGO-2% at high and low energy excitation.

The graphs of the decay profiles for ZnGO-2% follow in a similar fashion as above for Zn(OH)$_2$. The two distinct emission profiles of ZnGO-2% is shown in figure 4.5. With resonant absorption above the bandgap the emission shows a clear maximum near 580 nm, and for excitation below the bandgap the emission changes, like Zn(OH)$_2$, to a spectrum peaked near 500 nm, which is the normal defect emission of ZnO. Unlike ZnO, the changes in the emission profile do not occur at the band edge emission wavelength, but rather the emission profile is robust until nearly 410 nm. The multidimensional time decay characteristic are shown in figure 4.6 for six different emission regions (400, 520, 560, 600, 640 and 680 nm). Each curve is normalized to the maximum value for comparison. Contrary to the case of Zn(OH)$_2$ there is no excitation excitation near 415 nm is not an additonal excitation pathway which is attributed to the lack of the Zn vacancy sites in the GO composites and the fact that the GO is the
lowest energy level where the energy ends up, so excitation into a tightly bound
defect state of the Zn matrix would not necessarily lead to emission of the GO.
The time decay profiles are similar for all emissions except the 400 nm ZnO
bandedge emission. The long lifetimes are obtained for excitations between
370 and 410 nm excitations. It is clear that resonant absorption at 390 nm
produces the longest lifetimes which is indicative of energy transfer from the
Zn matrix to the GO matrix to produce long lived states that persists for
nanoseconds. Additionally, with higher energy excitation below 370 nm where
the ZnO is not resonantly excited, there is not a long emissive state as seen
in the Zn(OH)$_2$, again indicative that if the observed emission is from the GO
network, then non resonant absorption of the ZnO would not result in effective
energy transfer from the Zn to the GO regions.
Figure 4.6: Time decay plots of ZnGO-2% for different emission bands.
4.4 **Effects of Defects**

In the case of both Zn(OH)$_2$ and ZnGO the emission profiles and time decay profiles are not what one would expect from a single resonant absorption of the Zn phase. The observation that there is considerable emission with energy lower than the band gaps determined by the Tauc plots implies that the defects and surface states of the molecular clusters are very photoactive. Zn(OH)$_2$ displays a similar excitation profile to that of ZnO in the high energy region, but the emission profile is stable past 400 nm which means that the exciton state of the ZnO phase is not the dominant decay route in the material. These excitonic states feed into the photoactive defect states as is seen by the ultrafast decay of the 400 nm emission in all cases except for neat ZnO nanopowder.

Additionally, the same excitation profile observed with sub gap excitation energy means that the defect states are the final excited state of the composite and that they can also be directly excited. The 2D excitation-emission scans discussed in chapter 2 show that the Zn(OH)$_2$ shares similar defect levels as does ZnO. The time resolved excitation-emission scans in this chapter confirm this effect as well, in that the Zn vacancy defect can be excited near 415 nm to produce the longer wavelength red defect emission. The effect of GO is seen by considered the 3D excitation plots in figure 4.6. There is no obvious effect of any electronic state near 415 nm, and all the time decay profiles show the longest lifetimes for excitations between 375-400 nm, while still lower energy than the ZnO bandgap, is inclusive of the shallow defect levels of the composite which when directly photoexcited lead to long lived emission indicative of efficient energy transfer to the low energy states of the composite.
Comparing the time decay landscape of Zn(OH)$_2$ to that of ZnGO-2%, the obvious difference is the single decay region of excitation in the GO composite versus the Zn(OH)$_2$. These measurement do not yet lead to accurate quantitative comparisons between the lifetime of the low energy states in each composite because of signal to noise and electronic effects. It is expected that mid range energy (400-450 nm) where the Zn vacancy defects are photoactive in absorption and emission would show shortened lifetimes in the GO composites versus Zn(OH)$_2$. The steady state spectra are identical for the two materials, and the low energy excitation produces the same defect emission for both. However the time decay excitation spectra show an additional excitation for Zn(OH)$_2$ which could have a faster decay component in the GO composites if this were an intermediate state in the energy transfer process. Even though the Zn vacancies need not be directly coupled to the surface states that could mediate the energy transfer, the lifetimes and intensity would decrease in the case that the hole, or entire exciton migrated to the GO matrix. A zinc vacancy could capture an excited electron, but in order to observe a luminescence, recombination with a hole must occur, so if the hole were able to leave the Zn matrix with the electron, the probability of recombination in the Zn vacancy defects would be reduced and the emission signal would change. The lack of 440 nm emission in the GO composites supports this, but on the other hand, the lack of excitation near 415 nm in the GO composites may be indicative the the ZnGO composites do not have many Zn vacancies. The more likely scenario is that the energy transfer into the GO is mediated either by the surface states and surface defects of the ZnO/Zn(OH)$_2$, or by resonant transfer of the Zn
unit directly to the GO phase. The steady state and time resolved 2D plots of Zn(OH)$_2$ show excitation profiles similar to neat ZnO. ZnGO-2% on the other hand does show the same steady state excitation profiles, but the time resolved 2D spectra of ZnGO-2% are not the same for the materials without GO. Higher energy excitations into the upper excited states of the Zn matrix do not produce long lived emissions of any wavelength. This may be due to the lack of coupling of the upper states to the surface or GO states. It is possible that a large number of excited electrons would change the electrostatic environment and decrease the effective coupling to the GO. In the ZnGO, both resonant absorption of the Zn matrix and excitation into the defect states of the Zn produce long lived luminescence of all wavelengths of the composite, and with a maximum lifetime near the emission band of the Zn phase.

The resonantly excited exciton in the lowest excited state of the Zn matrix would be delocalized over a large region of the Zn matrix. One of the energy landscape axes can be considered as an effective “distance traveled” axis for the excitation. In order for the Zn phase excitation to end up on the GO, it must leave the Zn matrix, cross the surface states and end up on the GO. This is considered to be in the hopping regime of energy transfer because there is little change in the absorption profiles of the composite materials versus their neat form, which means there are not additional states formed between the Zn and GO, however changes in the luminescence are a result in their interaction. It is through the surface states and defects of the Zn phase that the excitation must hop through, which is why both resonant excitation and lower energy excitation can both produce long lived emission in the GO composites, and
also why the excitation band of the Zn vacancies is not observed for the GO composites.

4.5 Future Work

The composite materials show a complex energy landscape and emission properties. Attempts were made to measure the time resolved spectra of higher concentration GO composites, but due to signal to noise and material inhomogeneity these measurements are not yet accurate. More careful measurements in controlled environments will then lead to a complete data set for comparison of varying amounts of GO in the composites to better understand the effect of the carbonaceous phase. Additionally, with accurate numerical measurements of the lifetimes and quantity of carbon, transfer rates into the GO should be attainable. Also, the abnormal spectra of GO are due more analysis. Chapter two describes an alternative model of GO in that as an indirect band gap material it is photoactive to very low energies. Experiments should be done with electrical and opto electronic responses of GO in the mid infrared range. Temperature dependent I-V measurements of GO alone should be able to confirm the nature of the band gap of the material. And if this were the case of a small band gap, small modifications of the GO would then lead to tunable low voltage organic electronics. The future experiment is thus to measure the I-V curves of a series of GO samples to better understand the defect nature of the GO itself and it would be very important to the scientific community to understand the proper way to analyze the photoactivity of nano carbon based systems with properties similar to graphene. As for the composite material, further time
resolved and polarization analysis across the energy landscape will give more information into the detailed nature of the energy transfer processes. Since the ZnGO composites show a robust excitation profile from 370-410 nm, low temperature measurements would be very helpful to determine precisely which defect states, or new states altogether, are mediating the electronic coupling.
You can make a solar cell from raspberries.

5

Solar Cell Devices

5.1 Introduction

The composite materials of Zn(OH)_2 with Graphite oxide were tested as sensitized solar devices as part of the thesis work. The large porosity of the composite makes it attractive to use it in a sensitized solar cell configuration as ZnO and TiO_2 are already well known materials that can make a low cost and low toxicity solar cell with a few percent efficiency. The major challenge
in this part of the thesis was to establish a fabrication protocol that produced functioning and consistent devices. Most critically, the ZnGO composites are highly insoluble in most solvents, and therefore do not have good adhesion or deposition properties with the conductive glass slides of indium-tin-oxide (ITO). However the composite material is photoactive and does display they typical I-V characteristics of a solar cell when functioning properly. Unfortunately, there were not enough functioning devices made and the fabrication was very material intensive. It is likely that the porous nature which is beneficial for sensitizing elements may also be adding a large number of defects and electron traps so that electrical conduction is not optimal even though the ZnGO composites exhibit enhanced photoactivity.

5.2 Solar Energy

The sun is a giant fusion reactor that outputs radiant energy. The energy spectrum that reaches earth and penetrates through the atmosphere is termed the air mass 1.5 spectrum. It is the product of the blackbody output spectrum of the sun near 5500 degrees Kelvin and the absorption spectrum of the atmosphere between the earth surface and the sun. It is peaked in the yellow region of the visible spectrum, however almost 50 Conventional silicon has a fundamental band gap near 800 nm which leads to absorption across the major part of the visible spectrum of the sun’s irradiance. While a higher band gap would lead to higher energy electrons (or higher voltages), less of the solar spectrum would be available for single photon conversion.

A thermodynamic detailed balance calculation using the parameters of the sun
and a single p-n junction solar cell with a fundamental gap of silicon leads to a upper limit near 30% efficiency of conversion. Later calculations were done for more numbers of junctions and in the theoretical limit of an infinite number of junctions the maximum solar to electrical conversion efficiency would be near 70% however, making these infinite junction cells is not easily obtainable and the theoretical efficiency is not reached due to inevitable impurities and therefore defect sites and scattering since these cells are based on long range order and energy bands in a crystalline material. Solar Cells are now classified by generation. First generation solar cells are based on high quality crystalline silicon p-n junctions. High quality refers to the long range periodic symmetry of the lattice and lack of defects. The interface between the p-type material and n-type material defines the electrostatic asymmetry. The charge asymme-
try in the materials results in the creates a depletion region at the interface where photoexcitation occurs. Second generation solar cells follow the same scheme as first generation, but is based on amorphous semiconductor materials. The lower symmetry of the amorphous material requires less energy input to create the solid state material and results in slightly reduced photo-voltaic conversion. Third generation solar cells, also known broadly as Graetzel cells, are based on light sensitization by a primary photo-acceptor and a separate energy acceptor. The overall scheme of energy conversion is similar to that of biological photosynthesis. The photosynthetic process uses a variety of dye molecules (chlorophyll and beta-carotene) to absorb sunlight and promote an electron into an excited state. From here, a series of downhill processes places
the excitation energy at a reaction center where the energy is transformed into a charge separated state and the associated electrical potential energy is used to drive a chemical process to make food for the plant. A sensitized solar cell uses a photoacceptor (dye or quantum dot) to absorb the sunlight and also promotes the electron of the primary acceptor into an excited state. This electron is pulled into a wide bandgap semiconductor oxide where it becomes a conduction electron. The surrounding bath must then replace the lost electron in the primary acceptor which then results in the charge separated state with the electron in the semiconductor oxide and a hole left over in the surrounding bath molecules. This potential energy can then be used as a current or stored in a battery. A major benefit of third generation solar cells is their ease and low cost of production. Their properties can easily be tuned with the modification of the constituent materials. Varieties of dyes or quantum dots can enhance the absorption spectra and modifications of the semiconductor oxide can improve the working voltage and conductivity of the solar cell.
Figure 5.3: Energy levels and real space schematic of a sensitized solar cell. A quantum dot (QD) is the sensitizer and light promotes the QD from its ground state $S$ to its excited state $S^*$ upon absorption of the photon. The excited electron can transfer to the conduction band of the metal oxide (ZnGO) to then power an electrical load. Simultaneously, the redox electrolyte refills the empty ground state of the sensitizer to prevent recombination of the QD, and the returning exhausted electron refills the electrolyte. The working voltage of these devices is limited by the difference in the redox energy level and the lower conduction band of the metal oxide. The yellow blocks are electrical contacts and the black layer on the counter electrode is a chemical catalyst to improve electron re-injection (graphite or platinum).
5.3 Solar Cell Device Fabrication and Performance

The architecture of a sensitized solar cell is described and demonstrated here. The device is a multilayered structure which is made up of (bottom to top) a solid substrate, a conductive coating on the substrate, the high semiconductor material sensitized with dye or quantum dots, an electrolyte layer to complete the redox cycle, a top transparent conductive coating and a top transparent substrate. The cells made in this thesis used soda lime glass with a thin layer of indium tin oxide (ITO) as the substrates and transparent conducting oxide. The electrolyte used was "Iodolyte" purchased from Solaronix which is an Iodine/tri-Iodine electrolyte liquid. The deposition of the semiconductor material is the most crucial part of the process. One particular method spreads a paste mixture of the semiconductor material onto the ITO. It is important to maintain a consistent thickness of the film for fair comparisons, and additionally there is some optimal thickness which would absorb as much light as possible while minimizing the resistive path length of the photo generated electrons. Figure 5.3 explains this method of fabrication. For the case of the ZnGO composite, because they are not soluble in any solution tried, the doctor blade method usually produced very uneven films and often would not result in full coverage of the ITO as parts would clump and pull of the slide. Any holes in the semiconductor film would result in shorting of the device and loss of signal and efficiency. An alternative method that was developed in this study was to spray the films onto the heated ITO substrate. In this way, a very thin and dense layer is formed. It is also possible to make transparent cells that could be used in windows. This method is a modification of spray pyrolysis.
Figure 5.4: The doctor blade method for fabricating sensitized solar cells. The pieces of tape act as a height spacer to make a thin film of the anode material of given width and height. Generally a smooth glass rod or tape covered blade will not adhere to the anode material. This method results in relatively thicker and uneven films due to the height of the tape spacers (microns) and inaccuracy during the spreading.

In the case of spray pyrolysis, the separate materials are directed to a heated surface where the thermally driven synthesis takes place. In the case of the ZnGO composties, it is already in its final molecular form, and the heated surface acts only to evaporate the carrier liquid fast enough to deposit a thin homogenous film of the metal oxide. The spray films, like the spread films, do not adhere well to the ITO and the sensitization step, soaking in the quantum dot or dye, would essentially wash the ZnGO material from the ITO.
Figure 5.5: Spray deposition of the anode material. The substrate is heated by a hot plate and the anode material dissolved in a common solvent is sprayed on with a spray nozzle attached to an inert gas tank. This method can produce thin and uniform films if the anode material is soluble in the liquid. Temperature ranges used in this work are between 250 and 350 °C. The distance to the substrate is approximately 10 cm.

Figure 5.6: Thin film of ZnGO2 made by the spray deposition method. The transparency is observed as the red color of the background signage seen through the film.
5.4 Efficiency Calculations

The power conversion efficiency of any process is simply:

\[ \eta = \frac{\text{Power}_{\text{output}}}{\text{Power}_{\text{input}}} \]

Since a solar cell is a photoactive diode, the region in which the device generates power is the fourth quadrant of the I-V curve. Under illumination the short circuit current should not be zero, and the open circuit voltage defines the maximum sustainable potential produced by the solar cell. For an ideal photodiode the I-V curve forms a rectangle in the fourth quadrant and the short circuit current and open circuit voltages are the points at which the product \( I_xV \) is maximum and thus the max power output of the ideal photodiode is

\[ \text{Power} = I_{sc}V_{oc} \]

In practice however the short circuit current and open circuit voltages will not be the points of maximum power production and the values \( V_{max} \) and \( I_{max} \) are read off from a power curve of the working diode under illumination. For ease of calculation and ease of understanding the difference from ideality, the fill factor is defined as

\[ FF = \frac{V_{\text{max}}I_{\text{max}}}{V_{sc}I_{sc}} \leq 1 \]

With this scaling value characteristic of the actual device, the efficiency can
be defined as

\[ \eta = FF \frac{V_{oc}I_{sc}}{Power_{input}} \]

Most relevant to solar cell devices is how they operate under natural solar illumination conditions. Therefore, a common standard is to use the AM 1.5 spectra of intensity $100\frac{\text{mWatts}}{\text{cm}^2}$. Using this intensity for solar cell testing, the efficiency is measured as

\[ \eta = FF \frac{V_{oc}I_{sc}}{\text{Intensity}_{light} \times \text{Area}_{light}} = FF \frac{V_{oc}I_{sc}}{100\frac{\text{mWatts}}{\text{cm}^2} \times \pi R^2_{spot}} \]

with R the radius of the excitation spot. Neglecting nonlinear effects, the spot size and incident power are only needed for standardization to the AM 1.5 spectrum, but computing the fill factor and the knowing the incident power one can compute the working efficiency of the device. It was found that for ZnGO composite materials sensitized with CdSe quantum dots a maximum efficiency of 1% was achieved. The project of making solar cell devices was then discarded due to low efficiency and lack of reproducibility with limited source material. Were a better fabrication method developed and if bulk material was available, these compounds should produce comparable efficiencies to other metal oxide sensitized solar cells. Additionally, the graphite oxide should be helpful in increasing conductivity and therefore overall short circuit current.


