Zinc Oxide Nanoparticles: Doping, Inkjet Printing, and Electron Accepting from Photoexcited Porphyrin Dyes

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Abstract

This research attempted to extend the useful applications of ZnO by investigating ZnO nanoparticles, doping ZnO nanoparticles, characterizing electron injection from dye molecules into ZnO nanoparticles, and depositing thin films of doped ZnO nanoparticles using inkjet printing.

Chapter 1 describes research that produced particles ranging from 2.7 nm to 1 µm of undoped and doped ZnO. These particles were made using solution methods with zinc acetate and aluminum and gallium nitrate salts as dopants, and the particles were characterized by ultraviolet visible absorption, photoluminescence, infrared absorption, and transmission or scanning electron microscopy. The doped ZnO nanoparticles displayed optical signatures of doping in particles larger than 10 nm. This is significant because doping of nanoparticles is still not fully understood, and there are few examples of successfully doping nanoparticles.

Chapter 2 describes the research done toward inkjet printing of ZnO films for potential use in a fully inkjet printed solar cell. The research aim was to produce a TCO film of ZnO using inkjet printing that had a bulk resistivity between $10^{-2}$ and $10^{-3}$ Ω cm, a thickness between 0.1 and 1 μm, the highest transparency possible, and processed using conditions under 250 °C. Film produced using solution methods including inkjet printing were characterized by four point probe ohmmeter, x-ray diffraction, ultraviolet visible absorption, visible microscopy, profilometry, and scanning electron microscopy. Inkjet printed films produced using nanoparticles did not meet the production requirements, but
progress towards these goals are presented along with the successes and shortcoming of the methods used.

Chapter 3 describes the research done on charge transfer from photoexcited porphyrin dyes into ZnO nanoparticles dispersions in methanol. The goal of this research was to further the understanding of the dye-semiconductor interaction and important electron transfer characteristics. Using a series of three porphyrin dyes and a range of particle sizes, the rate of electron transfer was investigated.
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Chapter 1:

This work focused on production and understanding ZnO films, nanoparticles, and doping, and is highlighted by the experimental observation that doped ZnO nanoparticles are one of a few materials that display air stable optical signatures of electronic doping, which were observed in particles as small as 13 nm and in particles larger than 100 nm. The particles produced range from 2.7 nm to 1 µm in diameter, and were characterized by ultraviolet visible absorption, photoluminescence, infrared absorption, and transmission or scanning electron microscopy.

1.1 Introduction

1.1.1 Zinc Oxide

Research was done on ZnO films, nanoparticles, and doping. Doping nanoparticles is a matter of significant research interest, and was investigated with a wide range of sizes. Electronically n- and p-type doping of bulk semiconductors is an important technology that is used in many applications, and expanding doping into nanoparticles is an important research goal.

Zinc oxide (ZnO) has been used in a wide range of applications: sun screen, window treatments, and as a transparent conducting oxide thin film.\textsuperscript{1,2} ZnO is a semiconducting material with the wurtzite crystal structure. It is transparent in the visible spectrum but absorbs UV light due to its 3.37 eV band gap. When n-type doped, it can also have a bulk resistivity of $10^{-3} \ \Omega \ \text{cm}$ using solution methods, which is within 3 orders of magnitude the bulk resistivity of silver.\textsuperscript{3-5} Despite having higher resistivity than many metals or doped semiconductors, ZnO is an important transparent conducting oxide...
(TCO) material for applications due to its visible transparency, semiconducting characteristics, and stability in atmospheric conditions.\textsuperscript{6} Important to many applications, ZnO is stable in atmospheric conditions in part because of its metal oxide composition. ZnO can also be produced using many precursors, synthesis methods, and conditions. Zinc and oxygen are also abundant, so ZnO is often relatively inexpensive to produce.

Due to fact that ZnO has the wurtzite structure and hexagonal symmetry, it has a c axis that is unique from other commonly seen growth directions.\textsuperscript{7,8} It has been observed that more rapid growth along the c-axis leads to nanorods and nanowires. Faster growth parallel to the a-b plane produces hexagonal sheets. Experimentally, this is accomplished using a highly basic synthetic solution, certain zinc salts, or certain additives and binders.\textsuperscript{9–16}

ZnO nanoparticles are relatively simple to synthesize using a variety of conditions and precursors. The two most common solution based ZnO nanoparticle synthesis methods are adding a base or water to a polar solvent solution containing a zinc salt, most commonly zinc acetate dehydrate. These two methods will be described later in more detail. Also, nearly monodispersed nanoparticles can be produced, which is not easily possible in other TCOs.\textsuperscript{16}

1.1.2 Doping

Both n- and p-type doped samples of ZnO can be produced. P-type samples are made using nitrogen, phosphorus, lithium, or sodium as dopants.\textsuperscript{17,18} However, undoped ZnO produced by most methods is intrinsically n-type,\textsuperscript{19} and n-type doping in ZnO is easier to achieve and produces samples with better conductivity than p-type doping. To n-
type dope ZnO, aluminum, gallium, and indium are commonly used dopants, but indium is used less often due to its relative cost and scarcity.\textsuperscript{20–26}

Doping of ZnO is often a simple process in many synthetic methods. Using identical conditions, deposition, and processing as non-doped ZnO sol-gel derived thin film samples, 1 to 5 atom % of dopant precursor such as Ga(NO$_3$)$_3$, Al(NO$_3$)$_3$, or AlCl$_3$ can often be added to the ZnO precursor solution and result in a doped film.\textsuperscript{27} This process will be discussed later in more detail.

Another important consideration when doping ZnO is whether the sample is zinc or oxygen rich, which corresponds to the redox state of the material. Starting from a material with an equal number of Zn$^{2+}$ and O$^{2-}$ ions, the material is oxidized or reduced if it becomes oxygen rich or zinc rich respectively.\textsuperscript{28–32} This can be done in processing of the material during or after synthesis or deposition. A reducing anneal at temperatures between 300 and 900 °C in 10% H$_2$ in N$_2$ is required to produce a conductive film in solution deposited ZnO.\textsuperscript{33–35} The reducing anneal can lower the bulk resistivity of the film by more than four orders of magnitude. This reducing anneal produces a zinc rich film and leaves behind electrons that fill trap states and put more electrons in the conduction band. Alternatively, when a ZnO film is annealed in air, it is oxidized, more oxygen rich, electrons are removed from the conduction band, and the resistivity of the film can go up by more than four orders of magnitude.

In nanoparticles samples, annealing at the temperatures used in films would fuse the particles together and make dispersing the particles difficult or impossible.\textsuperscript{36} In literature reports, oxidation or reduction of ZnO nanoparticles has been done chemically.\textsuperscript{37,38}
1.1.3 Doping Challenges in Nanoparticles

There have been several reports of doping and adding conduction band electrons to nanoparticles of ZnO\textsuperscript{37,39-41} and other semiconductors\textsuperscript{42-50}, but electronic doping of nanoparticles is not yet completely understood. Electronic doping of small nanoparticles is a significant challenge due to the relatively few dopant atoms and large surface area to volume ratio, which can react with the atmosphere or in solution to degrade a doped state. In a 3 nm ZnO nanoparticle, there are 590 ZnO units. A 3 nm nanoparticle that is 1 % doped would contain six gallium dopant atoms and has six possible conduction band electrons from those dopants. Because of the large surface area per volume ratio and relative high energy of these conduction band electrons, they are sensitive to redox chemistry by reacting with oxygen in the air or reducing something on the surface or in solution. The electrons may also not be in the conduction band due to an oxygen excess from the synthesis, charging of the particle, and surface trap states or defects. It is also possible that dopants would reside on the surface and not contribute conduction band electrons. All of these issues could contribute to small nanoparticles that may contain n-type dopant atoms but do not have electrons that reside in the conduction band.

Larger particles are more resilient to several of these issues. Dopants and electrons that are further within the nanoparticle would have less interaction with the surface and the surface to volume ratio may be significantly lower.
1.1.4 Quantum Confinement

When the radius of a nanoparticle is smaller than the exciton Bohr radius of the material, the particle is strongly quantum confined, which increases the band gap of a material and separates the conduction and valence bands of a semiconducting material into individual, quantized states. Nanoparticles can also be weakly quantum confined when the particle radius is slightly larger to the Bohr radius. Weakly quantum confined particles do have a small band gap shift due to the exciton being slightly confined but do not show quantized states. A diagram showing the effect quantum confinement is shown in Figure 1.1.\textsuperscript{51}

ZnO nanoparticles begin to be strongly quantum confined in particles of less than 6 nm in diameter. In the smallest particles used in the research (2.7 nm), the band gap is approximately 0.4 eV higher than bulk ZnO. A 6 nm nanoparticle has a much smaller band gap shift of 0.1 eV.\textsuperscript{52}

The band gap shifts were measured using ultraviolet visible absorption spectroscopy. Nanoparticle sizes were determined by examining band gap shifts using a literature method described in Chapter 3,\textsuperscript{52} and transmission electron microscopy was used to confirm the sizes of the particles.
Figure 1.1: (top) Representation of an exciton in bulk material, in a weakly quantum confined nanoparticle, and a quantum confined nanoparticle. (below) Representation of the effect that quantum confinement has on an exciton and the band structure of the material.
1.1.5 Optical Signatures and Characterization Methods

The optical characteristics of ZnO are well understood and often studied in literature because the optical properties of ZnO are important for its application as a TCO. There are several optical features that were important to this research: band gap shifts due to the Burnstien-Moss effect and quantum confinement, light scattering, photoluminescence, and infrared absorption.

Both the Burnstien-Moss effect and quantum confinement shift the band gap absorption of ZnO higher in energy. The Burnstien-Moss effect is caused by the filling of the bottom of the band gap with electrons, which moves the conduction band minimum to higher in energy.\(^{21,53}\) Quantum confinement, as described earlier, is an increase of the band gap caused by the radius of the particle being near the exciton Bohr radius.\(^{52}\)

Light scattering is a significant issue when particles are approximately one tenth the diameter of the wavelength of light, which means that a 40 nm particle can scatter blue light.\(^{54}\) Experimentally, light scattering is often seen in ZnO nanoparticles 20 to 30 nm. This is probably due to the fact that nanoparticle of that size often produce less stable dispersions, and agglomerates of a small number of particles would be large enough to scatter light.

Band gap photoluminescence of zinc oxide occurs after absorbing light with greater energy than the band gap. The excited electron can relax back to the valence band and emit light of slightly lower energy than the band gap energy due to a Stokes shift. ZnO samples also commonly emit a broad wavelength, green fluorescence after absorbing ultraviolet light. The exact mechanism behind this fluorescence is not totally understood in literature.\(^{34,55–63}\)
Lastly, two different infrared absorptions have been reported for ZnO in the literature. The first is an infrared absorption in undoped, quantum confined particles after a chemical reduction with sodium biphenyl.\textsuperscript{37,64} This chemical reduction filled trap states along with the first excited state of the quantized conduction band. A disappearance of the trap state emission was observed due to filling of the trap states. A bleach of the lowest energy portion band gap absorption was also observed, which corresponded to an electron being placed in the lowest energy quantized state of the conduction band. Similar to the Burnstein-Moss effect in non-quantum confined systems, this shifts the lowest possible band gap absorption to higher in energy. An infrared absorption attributed to a transition from between the lowest two energy levels in the quantized conduction band was also observed.

Another infrared absorption has also been reported in the literature for ZnO particles that were not quantum confined.\textsuperscript{65–69} A similar infrared absorption as also been reported for WO\textsubscript{3} and SnO\textsubscript{2} nanoparticles.\textsuperscript{70–72} The infrared feature is a characteristic for particles larger than the quantum confined regime that have been electronically doped and have conduction band electrons.

1.2 Experimental

1.2.1 Small Nanoparticles

Nanoparticle zinc oxide was synthesized using a modified literature method.\textsuperscript{73} A 5 mL solution of 0.552 M tetramethylammonium hydroxide pentahydrate in ethanol was added dropwise into a 15 mL solution of 0.100 M zinc acetate dihydrate in dimethylsulfoxide (DMSO) over several minutes. To produce doped particles, an
appropriate mole percent of the desired dopant, usually Ga(NO$_3$)$_3$ or Al(NO$_3$)$_3$, or AlCl$_3$, was added to zinc precursor in dimethylsulfoxide before the addition of the base solution in methanol. This produced particles that are approximately 3 nm in size. The reaction solution could then be heated to 65 °C in an oil bath with stirring if larger particles were desired. When heating the solution to make larger particles, the progress of the particle growth was monitored by periodically taking ultraviolet visual absorption measurements on aliquots taken from the reaction solution and tracking the shift of the band gap absorption energy. Using this method, particles could be produced up to approximately 6 nm in size where the band gap absorption no longer changes significantly with size and the particles enter the weak quantum confinement regime.

Once synthesized, the nanoparticles were precipitated with 40 mL of ethyl acetate, centrifuged for 5 minutes until the supernatant is clear, and suspended in a minimal amount of ethanol, approximately 5 mL. The particles were then precipitated a second time and suspended in methanol or ethanol.

1.2.2 Hydrolysis

In order to produce larger ZnO nanoparticles, a modified literature method was used, and 0.2 to 2.0 mL of 18 MΩ H$_2$O was added to a solution of 109.5 mg of Zn(ac)$_2$•2H$_2$O in 5 mL DMSO. If doped particles were desired, 0.13 to 3.9 mg of Ga(NO$_3$)$_3$ was also added to the water before mixing. Immediately after the water was added, the resulting solution was placed in an oil bath that has been pre-heated to between 100 and 180 °C and allowed to react for 0.5 to 30 minutes with magnetic stirring. The resulting ZnO nanoparticle dispersion was placed in a water bath to cool,
and 10 mL of ethyl acetate was added to precipitate the particles. After centrifuging the dispersion, the particles were collected and dispersed in ethanol or methanol.

Using a higher temperature, longer reaction time, or a larger volume of water would produce larger particles. Using this synthesis, particles ranging from approximately 10 nm to 1 µm could be produced depending on the synthetic conditions used. Three sets of particles were produced and characterized. The smallest set of particles were 12 nm in size when undoped and were produced using a 100 ºC oil bath, 0.2 mL H₂O, and a 10 minute reaction time. The next larger set of particles were 42 nm when undoped and were produced using a 180 ºC oil bath, 0.2 mL H₂O, and a 30 minute reaction time. The largest set of particles characterized were larger than 100 nm in size when undoped and were produced using 180 ºC oil bath, 1.3 mL H₂O, and a 10 minute reaction time.

1.3 Results and Discussion
1.3.1 Small Nanoparticles

Doped and undoped nanoparticles were produced with a range of sizes with the synthesis that uses tetramethylammonium hydroxide as a base. The ultraviolet visible absorption of undoped nanoparticles is shown in Figure 1.2. The particles in the image were calculated to be 2.8, 3.7, 4.9, and 5.4 nm in diameter using a method described in Chapter 3. Doped particles produced using this method did not show the optical characteristics of doping regardless of the particle size. However, all of the sizes of doped nanoparticles could be used to produce conductive films, which are described in Chapter 2. The films produced using the doped particles were several orders of magnitude higher
in conductivity than the undoped films. This result suggests that dopant atoms are present in or on the surface of the nanoparticles, and the lack of an associated optical absorption feature is probably due to the combination of the small size of these particles, relatively few dopants in each particle, and processing the particles in air. All of these factors are likely hindering the production of stable conduction band electrons. However, when a film is produced and annealed at high temperature, the structure of the film changes significantly and the dopant atoms are able to produce conduction band electrons in the film. These optical and film results confirm reports using a similar method.
Figure 1.2: Normalized ultraviolet visible absorption spectra of a range of ZnO nanoparticle sizes
**Larger Nanoparticle Doping**

Using the hydrolysis procedure modified from literature, particles ranging from 10 nm to 1 µm were produced. Useful nanoparticles smaller than 10 nm were not successfully produced with this synthesis. To produce nanoparticles smaller than 10 nm using this synthesis, the concentration of the zinc precursor needed to be decreased to the point where it was no longer possible to precipitate the synthesized nanoparticles from solution because their concentration was too low.

Larger particles were made by increasing the concentration of both the amount of zinc precursor, water, or reaction temperature compared to the original literature procedure. Doping of the particles was done by adding Ga(NO$_3$)$_3$ or Al(NO$_3$)$_3$ to the reaction solution as dopant sources. Several other dopant molecules were investigated, but nitrate salts produced the most stable particles that showed the best optical and film characteristics. Also, the addition of the dopant consistently decreased the particle size compared the undoped films. The sizes of the particles were measured using x-ray diffraction, which was verified by transmission electron microscopy or scanning electron microscopy depending on the size of the nanoparticles.

The nanoparticles produced by this method that were 12 nm in size when undoped showed several of the optical signatures of doping when doped with gallium. Characterizations of the particles are shown in Figure 1.3. The infrared absorption shows a clear difference between the sets of particles, and the infrared peak for the doped particles appears at 2300 cm$^{-1}$. These were the smallest particles produced using this method that showed an infrared peak using these methods.
Figure 1.3: (top) Transmission electron microscopy images of 1% doped 10 nm ZnO nanoparticles. (bottom) Infrared absorbance of doped and undoped ZnO nanoparticles.
A series of doped and undoped nanoparticles that were 42 nm in size were also produced using this synthesis, and the characterizations of the particles are shown in Figure 1.4. The doped particles had all three optical characteristics of doping. The infrared absorption feature of the particles shifted to higher in energy as the particles became more highly doped and therefore smaller. Light scattering can be seen for all the particles in the ultraviolet visible absorption graph. The undoped particles were the largest and scattered the most light, and the 3% doped particles were the smallest of the series and scattered the least amount light. The elemental analysis data are shown in parenthesis in the legend. It confirmed doping in the nanoparticles and was consistently lower than the dopant percentages present in the synthetic solution. This effect was most pronounced in the 3% doped particles, which contained only 1.77% dopant.
Figure 1.4: (top) transmission electron microscopy image of the 1% gallium doped ZnO nanoparticles produced in this series. (bottom) The ultraviolet visual absorption, photoluminescence, and infrared absorption of the gallium doped ZnO nanoparticle series. The particle size, gallium doping percentage, and gallium doping percentages from elemental analysis data are shown in the legend.
A set of nanoparticles larger than 100 nm was also produced with the hydrolysis method, and characterizations of the particles are show in Figure 1.5. An ultraviolet visible absorption measurement was not possible due to the particles scattering too much light, and the dispersions of the particles appear milky. There is an infrared absorption for the doped particles with a peak at 1500 cm$^{-1}$ that isn’t present in the undoped particles. However, the undoped particles have an absorption starting at 2000 cm$^{-1}$ that increases with increasing energy. This is most likely due to scattering because of the very large sizes of the particles. Infrared light of 3500 cm$^{-1}$ has a wavelength of 2.9 µm, and many of the particles shown in the scanning electron microscope image of the doped particles are 300 nm or larger, which is greater than the 10 % of the wavelength needed to scatter 2.9 µm light. Using this synthesis, the undoped particles have consistently been larger than the undoped particles, so it is likely that the undoped particles show significantly more scattering in the infrared region because they are larger than the doped particles.
Figure 1.5: (top) Scanning electron microscope image of the 1% gallium doped particles produced in this series. (bottom) Infrared absorbance for the doped and undoped particles in this series.
Along with the optical data, doping was confirmed on all the nanoparticles synthesized by hydrolysis with production of conductive films as described in Chapter 2. The doped films showed an improvement in conductivity of several orders of magnitude from the undoped films. However, due to the size of the particles, the films scattered a significant amount of light.

The production of doped particles near the quantum confined regime that show optical signatures of doping that are air stable is a significant result. Doping of nanoparticles is both a significant challenge and an active area of research, and these results show that these nanoparticles are both doped and have conduction band electrons.

1.4 Conclusion

Two synthetic methods were used to investigate ZnO nanoparticle doping: a method using tetramethylammonium hydroxide as a base and the other a hydrolysis method. Both methods were used to produce doped particles, which were used to produce conductive films with a significant improvement in conductivity from undoped films. However, only the non-quantum confined particles produced using hydrolysis showed air stable optical signatures of doping. The 10 nm doped particles are on the edge of the weak confinement regime, and show an infrared absorption. The series of larger nanoparticles that were 42 nm when undoped showed all three signatures of doping: a Burnstien-Moss shift of the band gap, a quench of the sub band gap photoluminescence, and an infrared absorption. It is likely possible to extend these result to produce stable conduction band electrons in ZnO nanoparticles smaller than 6 nm in diameter, but it would likely require a significant increase in synthetic and processing requirements.
Chapter 2

As part of a larger project to develop a process for producing a fully inkjet printed copper indium gallium diselenide (CIGS) thin film solar cell, inkjet depositing thin films of undoped and doped ZnO were investigated. ZnO is the n-type transparent conducting oxide layer in a CIGS cell, so ZnO’s resistivity and transparency are important in this application. Because inkjet deposition is done under ambient conditions and can be easily patterned, it has the potential of being an inexpensive alternative to vacuum deposition and lithography if the challenges of inkjet printing can be overcome. This is particularly important in solar cell production because the relative cost of solar cells is a major drawback hindering wider adoption of the technology. Additionally, it was a goal of this research to produce ZnO films with the required transparency and conductivity at temperatures at or below 250 °C, which is a critical temperature for maintaining high efficiency in CIGS solar cells. To achieve that goal, research was focused on the use of doped ZnO nanoparticles as an ink component. This chapter covers the progress towards inkjet printing of conductive ZnO thin films and shortcomings of the method used.

2.1 Introduction

2.1.1 Zinc Oxide Thin Films

Undoped ZnO is intrinsically n-type; however, its bulk resistivity is too high for use in many applications. ZnO’s bulk resistivity can be substantially reduced by adding n-type dopants, commonly aluminum or gallium. The deposition method used also affects the resistivity of doped ZnO. Vacuum deposition methods can produce films with a bulk resistivity as low as $10^{-4}$ Ω cm, which is approximately 100 times higher than the bulk
resistivity of silver. Solution based deposition methods produce films with higher bulk resistivity values in the range of $10^{-2}$ Ω cm to $10^{-4}$ Ω cm.27,75–80

Literature examples of solution deposited ZnO thin films are commonly annealed in two steps to produce films with low resistivity. First, films are annealed in air at temperatures from 500 to 900 °C for an hour, which can remove or decompose remaining solvent, counter ions, or impurities and increases the grain size of the film.81,82 The films are then annealed a second time in a reducing environment of 5% or 10% H₂ in N₂, a vacuum, or an inert environment. The second annealing step reduces the film, which changes the zinc to oxygen ratio in the film to more zinc rich. After the second annealing step, the resistivity of a doped ZnO thin film can be decrease by more than four orders of magnitude when compared to the nonannealed samples.83–85

One of the goals this research was to produce doped ZnO thin films at or below 250 °C, but if using those annealing temperatures could not produce the required bulk resistivity, the film should be produced at the lowest temperature possible. In solution based ZnO literature, there is no precedence for production of films at temperatures near 250 °C that have the required resistivity. Solution deposited films are commonly annealed at temperatures higher than 600 °C for two hours to reach a bulk resistivity of $10^{-2}$ to $10^{-3}$ Ω cm, which was resistivity required for use in the CIGS solar cells of this study.

To reduce the processing temperature, investigation focused on nanoparticles larger than 30 nm in diameter as part of the ink solution. This could potentially reduce the annealing temperature required because the particles begin with a similar grain size to annealed films with low resistivity, which is one of the reasons that annealing
temperatures in solution deposition methods are usually greater than 500 °C. Also, it may be possible to synthesize the particles to be zinc rich and not need as high of an annealing temperature in a reducing environment.

2.1.2 Solution Deposition Methods

Spin coating, dip coating, chemical bath deposition, and drop coating are the commonly used solution deposition methods to produce ZnO thin films. Spin coating is used often because it creates thin, regular films with a variety of precursors and solvents and uses simple instrumentation. It can also produce quality films with little optimization.

Spin coating was frequently used in this research because it could be quickly and easily test a variety of possible inks. Spin coating is done by depositing several drops of a precursor solution on the center of a substrate, and then spinning the substrate at speeds from 100 to 5000 RPM, which spreads the precursor over the surface and partially evaporates the solvent from the film. A heat treatment is then used to transform the precursor into ZnO, and then the process of deposition, spinning, and heat treatment is repeated until the desired thickness is obtained.

2.1.3 Inkjet printing

Inkjet printing is a solution based method in which a small volume of a liquid precursor is ejected from an inkjet device onto a substrate at frequencies up to 1-10 kHz, and has been used for the deposition of a variety of sol-gel and nanoparticle films. Inkjet printing devices are driven with a piezoelectric material or a small resistive heating
element. Several consumer printers use a heating element to vaporize a small amount of liquid in a small opening to eject a droplet. A piezoelectric driven inkjet printing head is also used in consumer printers and was used in this research because it is compatible with a variety of solutions with a wide range of boiling points and has few issues with clogging. Piezoelectric inkjet printing devices work by creating a pressure wave in a liquid by the expansion and contraction of a piezoelectric material, which forces a droplet out of an opening in the device. The droplets produced by the printing heads are approximately the diameter of the opening, which was 50 µm in size. Figure 2.1 shows the design of an inkjet device.
Figure 2.1 Diagrams of the inkjet device construction. (Diagrams modified from www.Microfab.com) The piezoelectric driver surrounds the capillary within the device.
A working set of driving voltage, pulse length, frequency, and reservoir pressure must be found to produce droplets from any new ink composition. Working parameters are often found and optimized by trial and error. Generally, the process of finding a working set of parameters starts by increasing the driving voltage until droplets are produced. The pulse timing is then adjusted until the droplets are regular and there are no satellite droplets. The frequency of droplet production is chosen based on the conditions and temperature of the substrate, the boiling point of the liquid, and the features that are desired. A frequency that is too high overloads the substrate with liquid, which often produces smearing or very irregular patterns. A frequency that is too low can cause issues due to printing on a dry substrate or simply wastes time. Once an initial set of parameters is found, they are optimized until the printing head can print for several hours without producing irregular or satellite droplets, clogging, or any other issues. An example driving voltage is shown in Figure 2.2, and literature simulated and experimental results for the device are shown in Figure 2.3. Figure 2.4 shows the effect of reservoir pressures on the printing orifice.
**Figure 2.2:** A example voltage and timing used to create droplets. The initial pulse of positive voltage contracts the capillary volume, and the device is given enough time to allow for the pressure wave to propagate and produce a droplet. The following pulse of negative voltage and twice the duration dampens the residual pressure waves in the device. The second pulse is not required to form droplets, but the device manufacturer suggests its use to prevent irregularities at high frequencies. (Graph modified from www.Microfab.com)
Figure 2.3: (a) simulated and (b) experimental droplet formation using deionized water and a 40 μm diameter inkjet head from Microfab. [Image modified from H. Wu et al.]
Figure 2.4: Three common positions for the meniscus in the inkjet orifice. The fluid pressure must be controlled to form a meniscus that is neither too positive nor too negative in order to assure droplet regularity. If the pressure is too high, droplet formation isn’t possible due to the opening wetting, which is shown in the bottom figure.
2.1.4 Ink Composition

The composition of the ink is vital both to ensure that the ink will work well with the inkjet device and to produce regular features on the substrate. There are several considerations that go into designing an ink’s composition. First, the ink must be stable in the inkjet device for several hours or days. Air sensitive chemicals or unstable colloids can’t be used or they would cause clogging in the device. The ink must also wet the substrate being used. Inks that have large contact angles with the substrate often collect into larger droplets, which go on to make any feature very irregular due to inconsistent drying. The ink must evaporate on the substrate at an appropriate speed, which is mainly affected by the temperature of the substrate and boiling points of the solvents used. Inks that evaporate too quickly can clog the printing device by evaporating at its small opening. Inks that evaporate too slowly can overload the substrate with liquid, which produces irregular features due to streaking on the substrate. The device manufacturer also reports that the viscosity of the ink must be less than 40 centipoise, approximately the viscosity of vegetable oil, or the device will not function correctly. An ink should also be designed to contain a workable concentration of film precursor: too much precursor can cause printing and drying issues and too little precursor will lead to slow deposition.

In designing an ink and finding a corresponding substrate temperature, the ink drying in the coffee stain pattern is a persistent issue that must be considered. Coffee stain patterning is characterized by a majority of the deposited material migrating to the outer edges of the produced features during solvent evaporation, which produces a drying pattern similar to the stain that is left on a table when coffee dries. This produces
irregularly shaped, undesirable features. To produce more regular printed features, the temperature of the substrate is usually heated to within a few degrees Celsius of the boiling point of the solvent, which greatly reduces the effect. This process can be seen in Figure 2.5.
Figure 2.5: A literature example of the coffee stain issue with inkjet printing. These data were collected on colloidal gold deposited from terpineol, which has a boiling point of 219 °C. The left images are atomic force microscopy (AFM) images of the surface. The middle graphs show AFM cross-sections of the AFM images at left. The images at the right are optical reflection images of the inkjet printed features. When the substrate is significantly colder than the boiling point of the solvent (shown at top), the coffee stain pattern dominates and the material migrates almost completely to the outer edges. At higher temperatures near the boiling point, the material is more evenly distributed in the feature, which is shown in the middle and bottom of the figure. (Figure modified from Ko, et al.)
2.1.5 Resistivity

Resistivity is a measure of how difficult it is for electrons to flow through a material when a voltage is placed across it. Resistivity is the inverse of conductivity, which is defined in Equation 1.

\[
\text{conductivity} = \frac{1}{\text{resistivity}} = \text{electron charge} \times \text{mobility} \times \text{carrier concentration}
\]  

Equation 1

Mobility and carrier concentration and therefore resistivity are directly related to film morphology, composition, and structure. Mobility is a measure of how freely conduction electrons move in a material. This value is dependent on the grain size of the material, the grain boundary characteristics, defects, and the number and properties of impurities. Inkjet printing and other solution deposition methods produce films that are polycrystalline. To increase mobility in the films, grain sizes are made as large as possible with a combination of deposition methods and annealing.\textsuperscript{113,114}

Carrier concentration is the other property that dictates the conductivity of the film and is a measure of the number of free conduction electrons in the film. The number of free electrons is affected by the doping, film processing, and the number of defects, traps, and grain boundaries in the material. This value is increased by optimizing the doping of the material and annealing the film in a reducing environment.

In thin films of a uniform thickness, sheet resistance is often the property that is measured and reported. It can be measured using a two or four point resistivity measurement. Once the sheet resistance is known, it can be converted to bulk resistivity, an intrinsic property of the material, by multiplying by the film thickness.
2.1.6 AC Resistivity Measurements

ZnO thin films sheet resistance was measured in this research using a four point probe. The instrument consists of four equally spaced electrical contacts in a linear arrangement that usually span 1 cm in length, which is shown in Figure 2.6. On the outer two contacts an alternating current was applied, which avoids charging and ionic conduction issues that happen when a direct current is used. The alternating current produced on the outer contacts is slowly decreased from 100 kHz to 1 Hz during the measurement. The instrument measures voltage at the inner two contacts, which is used to determine sheet resistance. The measurement is independent of contact resistance between the probe and film due to the voltage being read at the inner two contacts, which are not involved in producing the current.\textsuperscript{113,114}
Figure 2.6: Diagram of a four point probe setup. The outer probes work together to drive a current through the material, and the inner two probes measure the voltage difference between their positions on the material.
2.2 Experimental

2.2.1 Profilometry

Film thickness was measured using a Tencor P10 Profilometer. Thickness of inkjet printed features was measured with no further sample preparation. Thin film samples were selectively etched before thickness was measured. This was done by covering a portion of the film with tape and etching the uncovered portion of the film with a hydrochloric acid solution. The tape was then removed from the film, and the film was washed with ethanol and water before the measurement was done.

2.2.2 X-Ray Diffraction

X-Ray diffraction measurements were taken using the Bruker-AXS microdiffractometer. The instrument was calibrated using a LaB₆ standard before data collection, which allowed for grain sizes of the films to be calculated using the Scherrer line broadening feature of the JADE diffraction fitting software. Data fitting allowed for grain size to be calculated for grain sizes up to 100 nm. Also, analysis of the diffraction data allowed for identification of film orientation, which is common in ZnO thin films.

2.2.3 Photographs

Photographs of droplets were taken using a SCT-400HOL camera from Sentech interfaced to an InperX Inc. controller and a computer. Two different strobos were constructed for use as a camera flash. A one to four millisecond timing circuit and ultrabright LED were used as the first strobe, and the second was a modified flash from a Kodak disposable camera, which was built from a procedure reported in MAKE
magazine. This setup was used to estimate droplet size and speed and characterize issues with irregular droplet shape.

2.2.4 Spin Coating Solution Precursors

Two drops of the precursor solution were deposited onto a cleaned glass substrate, which was then spun at 3000 RPM for 30 seconds. The substrate was then heated to 300 °C for 10 minutes to form ZnO from the e precursor. This process of depositing, spinning, and heat treating was repeated until the desired thickness was obtained. The film was annealed in air at 600 °C for 1 hour followed by annealing at 600 °C for 1 hour in an atmosphere of either 5 or 10 % H₂ in N₂.

The solutions used in spin coating were modified from literature. Solutions of 2-methoxyethanol containing 0.35 M zinc acetate dehydrate, 0.35 M ethanolamine, and 3.5 mM of either aluminum chloride or gallium nitrate were prepared and then heated to 60 °C for 2 hours. Quartz and Corning 1737 glass were both used as substrates because both can be annealed at 600 °C without deformation. Substrates were cleaned with DI water, ethanol, and then dried with air before use.

2.2.5 Inkjet Printing

Inkjet printing required a printing device, a 50 μm orifice Microfab inkjet head (MJ-AB-01) with controller (Jetdrive III), and a device to move the substrate in two axis, a stage with two linear actuators (Newport 850B) and motion controller (Newport MM3000). Both of these devices were interfaced to a computer using labVIEW from National Instruments. A heating element was attached to the two axis stage, and the linear
actuators attached to the stage were programed to move in a snaking pattern, which could be operated at a wide range of speeds.

Several different ink solutions were tested and optimized. First, isopropanol was inkjet printed using parameters from Microfab, the inkjet device manufacturer. The system was also tested with a consumer ink designed for HP printers and a literature liquid-based zinc oxide ink made from an ethanol solution of 0.5 M Zn(Ac)$_2$·H$_2$O with 5% by volume of both ethylene glycol and glycerin. $^{116}$ These were deposited onto paper and microscope slide glass respectively.

2.2.6 Nanoparticle Inks

Doped nanoparticles were produced using the methods described in Chapter 1. Small nanoparticles were suspended in ethanol or 2-methoxyethanol for use in solution deposition, and the concentrations of the particles were changed based on the deposition used.

For the larger set of nanoparticle produced using hydrolysis method, hybrid solutions of nanoparticles and the solution precursor used in spin coating that contains zinc acetate, ethanolamine, and AlCl$_3$ were prepared and used for drop coating and inkjet printing. The solution used for inkjet printing was prepared using 7.5 mL formamide, 2.5 mL 2-methoxyethanol, 20 mg of 50 to 100 nm 1 % gallium doped ZnO nanoparticles, and 13.5 mg Zn(ac)$_2$·2H$_2$O with (1 % dopant) 0.16 mg Ga(NO$_3$)$_3$. The sol-gel component in this mixture was designed to be 25 mole % of the total ZnO after decomposition. This ink is stable for several days.
2.3 Results and Discussion

2.3.1 Zinc Acetate Thin Films

Research began with production of spin coated films because they are well known in literature and easily produce quality films, which were used to study ZnO thin film production, annealing, and manipulation as well as confirm and calibrate instrumentation and characterization techniques. Using the modified literature procedure given above, a spin coated film was produced and measured using profilometry to be 153 ± 13 nm thick. Using a four point probe, the film’s sheet resistance was measured after each processing step. The film’s sheet resistance was 5.0 ± 3.3 MΩ after spin coating and decomposing the precursor in air at 300 ºC for 10 minutes, 1.1 ± 0.3 GΩ after annealing in air at 600 ºC for 1 hour, and 5.2 ± 0.8 kΩ after annealing in a 10 % H₂ in N₂ at 600 ºC for 1 hour. Using the film’s thickness and sheet resistivity data, the bulk resistivity of the final film was calculated to be 8.0 ± 1.9 x 10⁻² Ω cm. Ultraviolet visible absorption spectrum for the film is graphed in Figure 2.8, which shows clear Burnstein-Moss shift of the band gap absorption after annealing in a reducing environment. The film’s x-ray diffraction data is shown in Figure 2.7.

The (002) is the only miller index that diffracts because the film grew oriented with this crystalline plane perpendicular to the substrate. This direction is the most polar face of a ZnO crystal, and often the fastest growing. Literature reports have attributed the oriented growth pattern of this film in part to the ethanolamine ligand used in the production of these films.⁹¹
Figure 2.7: X-ray diffraction data taken on the zinc acetate spin coated film. From left to right, the three vertical lines represent the placement of ZnO’s (100), (002), and (101) miller indices.
Figure 2.8: (bottom line) Ultraviolet visible absorption spectra of the blank substrate, (right peak) the doped ZnO film after annealing in air, and (left peak) the same film after annealing in a reducing environment. As shown, the films have a noticeable absorption when compared to a blank substrate in the visible spectrum (400 to 750 nm).
Films produced using this method did have a higher visible light absorption and bulk resistivity than reported in literature, but they were a good starting point for further investigation. The properties of the films were close to the requirements for CIGS solar cells, but they were annealed at 600 °C, which is much higher than the goal temperature of 250 °C.

2.3.2 Small Nanoparticle Thin Films

Thin films were produced by spin coating using the nanoparticles produced by the synthesis method described in chapter 1. Shown in Figure 2.9 is an experiment that was done to compare the zinc acetate spin coating method and spin coating doped nanoparticles.
Figure 2.9: (left) X-ray diffraction and (right) resistivity data for (top) sol-gel aluminum doped ZnO and (bottom) nanoparticle aluminum doped ZnO thin films. The graphs on the left show the evolution of the x-ray data with increasing annealing temperatures. The (100), (002), (101), and (102) are the commonly seen planes in ZnO diffraction data, and are indicated at top with arrows. On the right, the grain size of the films calculated using the (002) plane and the bulk resistivity of the films are shown.
The data from the experiment shown in Figure 2.9 shows slightly larger grain sizes from the sol-gel method when comparing equal temperatures. The sol-gel film is an ordered film as discussed earlier, and the nanoparticle film shows each of the expected planes. The bulk resistivity also followed the same trend between both samples with the exception of the 500 °C anneal on the nanoparticle film. From this and other experiments, the nanoparticle films were found to degrade after annealing in 5 or 10% H₂ in N₂. Films annealed at 600 °C would lose approximately 100 nm of thickness in an hour. There was a metallic looking residue that formed on the cooler ends of the annealing tube, which was likely metallic zinc from the film.

2.3.3 Large Nanoparticle Thin Films

Investigation shifted lastly to producing films using the larger sets of particles, which were 30 to 50 nm in size. This size range was chosen because ZnO nanoparticles larger than 50 nm in size weren’t stable in solution for long enough for use in inkjet printing and nanoparticles smaller than 30 nm in size don’t have large enough initial grain sizes to produce low resistivity films without high temperature annealing.

Investigation focused on solution deposition of a hybrid of nanoparticles and zinc acetate. Deposition of larger nanoparticles has two significant drawbacks that a hybrid deposition could potentially solve: light scattering and higher resistivity in a porous film. A hybrid deposition would hopefully lower the porosity of the film by filling in the spaces between the nanoparticles, which could decrease the resistivity of the films substantially. Also, nanoparticles of this size and films made from them scatter a
significant amount of light. If the spaces between the particles are filled, much more transparent films could be produced.

Drop coating was used to test these films before they were inkjet printed. The films produced are shown in Figure 2.10. The films made with 30 and 50 nm ZnO nanoparticles showed a significant decrease in resistivity when up to 20 % by weight sol-gel precursor was added. It can be seen from the scanning electron microscope images that the films that contained sol-gel precursor were less porous.
Figure 2.10: (top) Scanning electron microscope images taken on films made with (top left) 30 nm and (bottom left) 50 nm nanoparticles and a hybrid mixture of 20% by weight sol-gel precursor with (top right) 30 nm and (bottom right) 50 nm nanoparticles. (bottom) Graph showing the effect of the addition of a sol-gel precursor to the sheet resistance of drop cast films made with 30 and 50 nm nanoparticle.
2.3.4 Inkjet Testing and Optimization

The conditions used in the inkjet printing needed to be tested and optimized. Voltage, timing, and reservoir pressure affect whether droplets can be produced, the regularity of the droplets, and the size and speed of the droplets. Reservoir pressure was the first thing optimized, and photographs of example reservoir fluid level effects are shown in Figure 2.11. If reservoir pressure is too high or low, the fluid in the inkjet head does not match the tip of the device, which prevents droplet production. Once a working reservoir pressure was obtained, the voltage and timing used to dispense the droplets could be optimized. Isopropanol was the first liquid tested, and it was found to print at frequencies from 10 to 1000 Hz using a 40 μs pulse at 40 V followed by a 80 μs pulse of -40 V, which matched the manufacture’s recommendations.

A consumer inkjet printer ink was deposited onto paper using the setup, and the results are shown in Figure 2.12. The picture shows the snaking pattern used in later experiments, but in the bottom line there is a slight error with the snaking pattern producing a triangle edge instead of square edge, which was fixed to a square edge by changing the pattern instructions.
Figure 2.11: Images of the effect that reservoir pressure has on the fluid level of the inkjet device’s capillary tip. The liquid used was neat isopropanol. Three possible reservoir pressure scenarios are shown: (A) an air bubble in the inkjet head caused by too little pressure, (B) a droplet on the inkjet head caused by too much pressure, and (C) an inkjet printing at 2 kHz when a working reservoir pressure is used.
Figure 2.12: A picture of a black ink deposited onto paper using the Microfab inkjet head. The top and bottom were drawn with the same snaking pattern at a jetting frequency of 1 and 5 Hz respectively. These features are 1 cm long, and they were made by moving the inkjet head at 1 mm/s.
2.3.5 Photographs

A flash circuit modified from a Kodak disposable camera was built and tested. Earlier attempts at using an ultra-bright white LED and a timing circuit were unable to produce photographs with enough brightness to resolve droplets. As seen in Figure 2.13, the modified flash allowed for pictures to be taken of isopropanol droplets. The images show examples of regular droplets and some of the issues with irregular or satellite droplets that can be produced when the voltages and timings conditions are not fully optimized.

Although the droplets are visible in these pictures, they are streaked because the flash timing was too long, approximately 10 ms in length. Unfortunately, the flash length could not be reduced or tuned with a circuit due to the high voltage and amperage inherent in a flashbulb. The photographs are single illuminated frames from a 30 frame per second movie created using a camera and a flash bulb 15 cm from the inkjet head at a 90° angle from the camera. The photographs are grainy due to the quality of the camera.

These tests and optimizations laid the groundwork for the rest of the investigations. After much trial and error, the inkjet system could be used with a number of different inks and print for hours or days without issues.
Figure 2.13: Photos of a droplet production from an inkjet head. The images were taken with a (top) 1 kHz and (bottom) 2 kHz jetting frequency respectively. The end of the inkjet head is at the top of the images, and the streaked bright objects down the middle are isopropanol droplets. The upper left photograph is an example of regular droplets. The other three pictures are examples of irregularly shaped and satellite droplets.
2.3.6 Inkjet printing Zinc Acetate

In an attempt to inkjet print the solutions used for spin coating, it was found that 2-methoxyethanol, the solvent used in spin coating zinc acetate precursors, does not wet the surface of glass well enough for it to be compatible with inkjet printing. Printed droplets of this solution would shift and combine into larger droplets. When heated, these droplets would crack and turn black. However, if the solution contained 50% isopropanol, the ink was able to wet glass substrates.

It was also found that solutions of 0.35 M zinc acetate created features with a large amount of cracking. To relieve this, the concentration of the precursor was reduced, which eliminated the cracking issues. As shown in Figure 2.14, inkjet printed features created with a 0.05 M solution of zinc acetate had no cracking in the middle of the features but significant light scattering on their edges. This was caused by precursor migration to the edges of the features due to coffee stain patterning. The film’s features were measured using profilometry to be between 150 and 300 nm thick on their edges and less than 30 nm in the center of the features.

It was disappointing that the precursor used for these experiments produced films with significant light scattering on their edges. This could potentially be reduced or eliminated by raising the substrate temperature to within a few degrees from the solvent’s boiling point. However, the investigation shifted towards nanoparticle precursors due to potential benefits of those inks.
Figure 2.14: An image of an inkjet printed film produced using a sol-gel precursor ink that shows significant light scattering on its edges. It was produced with a substrate speed of 1 mm/s at a 5 Hz jetting frequency.
2.3.7 Nanoparticle Precursors

Nanoparticle inks were tested due to several possible advantages they have in film production. Using a dispersion of nanoparticles that were 3.2 nm in diameter, inkjet printed features were deposited onto glass substrates. The films and lines produced with the small nanoparticles all had excellent transparency, and could be produced with minimal coffee stain issues. However, as shown from spin coating studies, the resistivity of small nanoparticle films is higher than the requirements, so investigation focused on inkjet printing of hybrid solutions of larger nanoparticles and zinc acetate that were shown to produce films near the resistivity requirements when drop coated.

The images in Figure 2.15 of lines that were produced using hybrid inks show that the substrate is covered with a thin layer of ZnO from the zinc acetate in the ink and there are single and agglomerated 50 nm nanoparticles that are spaced throughout the feature. It appears from these images that there is no significant coffee stain patterning in these features, which was confirmed with profilometry. Using the same conditions as the lines shown in Figure 2.15, seven layers were deposited to form a film that was characterized in Figure 2.16. The images show that many of the individual particles have combined into a larger material with the zinc acetate precursor filling the spaces between the particles, which produce a more dense structure that is desirable for conductivity. A second film was produced and characterized in Figure 2.17. The film was heat treated at 300 ºC after each deposition, and then annealed in 10 % H2 in N2 for 1 hour at 400 ºC after all depositions were finished. With a
two point probe, the film was measured to have a resistance between 80,000 to 400,000 Ω over a 1 cm distance.
Figure 2.15: (top) Visible light microscopy and (middle and bottom) scanning electron microscope images of an inkjet printed line produced with an ink containing a hybrid of 50 nm nanoparticles, zinc acetate, and Ga(NO$_3$)$_3$. The line was deposited at a 10 Hz inkjet frequency, a 0.8 mm/sec substrate speed, and a 130 °C substrate temperature. The film was heat treated at 300 °C for a few minutes after the deposition. The scanning electron microscope images were taken in the (middle) middle and (bottom) edge of the line.
Figure 2.16: Scanning electron microscopy images of inkjet printed films produced using seven passes of the conditions used in Figure 2.15.
Figure 2.17: Scanning electron microscope images of a film made from 5 depositions using a 50 Hz inkjet frequency, a 0.8 mm/sec substrate speed, and a substrate temperature of 155 °C. A platinum coating was not used to produce these images as is normally needed because the film was electrically conductive enough to not require one.
2.4 Conclusions

Films produced using spin coating, drop coating, and inkjet printing were made from zinc acetate, nanoparticle precursors, and a hybrid of the two. This was done in investigation towards inkjet printing of a transparent conduction oxide film of ZnO for use in CIGS solar cells. Films produced using sol-gel methods with zinc acetate as a precursor matched well with literature examples, but had higher visible light absorption and resistivity. Film produced using small 3 nm nanoparticles had great transparency when spin coated or inkjet printed. However, when these films were annealed in a reducing environment above 500 °C, they showed significant degradation. This greatly limited their use in this application and films could not be produced within the resistivity requirements. Inkjet printing hybrid films containing doped 50 nm, zinc acetate, and Ga(NO₃)₃ showed promising results for producing films that were transparent and conductive. The inkjet printed hybrid films showed good resistivity, but optimization and further experimentation was not finished on producing transparent and conductive hybrid films. It is likely possible that further optimization on this inkjet printing method could produce films with the required transparency and conductivity.
Three porphyrin dyes were synthesized and their excited state charge transfer with zinc oxide nanoparticles was investigated. The 5-(4-carboxyphenyl)-10,15,20-tris(4-di-4-tolylaminophenyl)porphyrinatozinc (II) (ZnDTAP), 5-(4-carboxyphenyl)-10,15,20-tris(2,4,6-trimethylphenyl)porphyrinatozinc (II) (ZnP), and 5-(4-carboxyphenyl)-10,15,20-tris(4-cyanophenyl)porphyrinatozinc (II) (ZnCNP) dyes were designed to span a range of excited state potentials. The dyes’ binding constants and electron transfer rates to quantum confined ZnO nanoparticles were measured in methanol as a function of the size of the ZnO nanoparticles. The conduction band potential and band gap both increase with decreasing nanoparticles size due to quantum confinement. Several characterizations were done to determine the effect of changing the dye and nanoparticle size: ultraviolet visible absorbance and photoluminescence studies were used to construct Stern-Volmer plots and Langmuir isotherms, electrochemical studies allowed the estimate of the excited state potential for each of the dyes, time correlated single photon counting was used to determine electron transfer rates, and calculations were done to determine the HOMO and LUMO of the molecules.

3.1 Introduction

3.1.1 General

Molecular sensitizers for use in solar cells have been a research topic of resent interest and challenge. Ruthenium polypyridyl complexes and zinc based porphyrin molecules have been a focus of research. Molecular sensitizers in photovoltaics are attached to TiO₂ or ZnO.
and undergo a photoinduced electron transfer from the photoexcited dye molecule into the metal oxide. Grätzel has shown Ruthenium sensitized TiO$_2$ solar cells can have power conversion efficiencies up to 11.5\%.\textsuperscript{123}

There are several considerations and issues that must be addressed in constructing high efficiency dye sensitized solar cells, and it was the goal of this research to understand the photoinduced electron transfer between porphyrin molecules and ZnO. Specifically, changes to the phenyl groups attached to the porphyrin core were made to alter the excited state energies of the porphyrin molecule. This research presents the changes to photoinduced electron transfer as measured by steady-state photoluminescence and time correlated single photon counting.

3.1.2 Porphyrin Dyes

Three zinc porphyrin dyes were synthesized and used in these investigations, which are shown in Figure 3.1. All three dyes have a carboxyphenyl group that can bind to ZnO. The ditolylaminophenyl, trimethylphenyl, and cyanophenyl groups used in the three dyes were chosen because the ditolylaminophenyl group is electron donating, the cyanophenyl group is electron withdrawing, and the trimethylphenyl group is a commonly used group with porphyrin molecules that lies between the other two groups in electron donation. The electron donation from the groups connected to the porphyrin core change the excited state potential of the dye, which was important for measuring the energy dependence of electron injection.
Figure 3.1: The three porphyrin dyes used in these experiments
3.1.3 Size Calculations

The size of the ZnO nanoparticles was determined using a literature method.\textsuperscript{52} The conversion between band gap shift and diameter is shown in Equation 3.

\[
\Delta E_g = 100(18.1d^2 + 41.4d - 0.8)^{-1}
\]  (3)

The change in band gap, \(\Delta E_g\), is given by the difference between the inflection point of the absorption and that of bulk ZnO (3.3 eV) in units of eV. The diameter of the particles is given by \(d\) in units of nm.

For these experiments, particles were grown to approximately 2.8, 3.6, 4.7, and 5.4 nm in diameter to span most of the conduction band energy range possible by changing ZnO nanoparticle diameter. Also, using data from literature, it was concluded that for this study 75\% of the change in band gap was considered a change in conduction band energy, which can also be calculated using the effective mass of the electron and hole in ZnO.\textsuperscript{7}

3.2 Experimental

3.2.1 ZnO synthesis and size calculations

The ZnO nanoparticles of various sizes that were used in this study were synthesized as described in chapter 1. All of the particles used in the quenching studies were undoped, and particles were made ranging from 2.7 to 5.4 nm in size.
3.2.2 Transmission Electron Microscopy

TEM images were acquired on an FEI Tecnai G² F30. The ZnO nanoparticles solutions were diluted with methanol, and a drop of the diluted ZnO solution was placed on an ultrathin carbon on holey carbon support film from Ted Pella and allowed to dry.

3.2.3 Photoluminescence

Steady state photoluminescence measurements were taken on a Spex Fluorolog 1680 0.22 m double spectrometer using a xenon lamp. Measurements were taken in a 1 cm cuvette using front face geometry, and photoluminescence intensities were corrected for the instrument sensitivity, which was determined using a known series of dyes.

3.2.4 Porphyrin Synthesis

The three porphyrin molecules were synthesized using a modified literature method in collaboration with Raghu Chitta.\textsuperscript{166} The specific synthetic values given below are those used for the synthesis of ZnCNP.

All the solvents and chemicals used were reagent grade quality, purchased commercially, and used without further purification unless otherwise noted. Figure 3.2 is a diagram of the synthesis steps. The three porphyrin molecules with carboxylic acid groups were all synthesized by condensation of pyrrole with the corresponding phenyl aldehydes in the presence of BF\textsubscript{3}·etherate. The reaction was completed by the addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) followed by triethylamine. The porphyrin ester was base hydrolyzed in a THF and water solution and then acidified. The
resulting carboxylic acid porphyrin was treated with zinc acetate dihydrate to form the final porphyrin. All of the porphyrin molecules were characterized by H\(^1\) NMR.

The initial reaction to form the porphyrin consisted of a 1.0 L CHCl\(_3\) solution containing 1 equivalent 4-formyl benzoate (0.400g, 2.44 mmoles), 3 equivalents of the desired phenyl aldehyde (0.96g, 7.32 mmoles 4-cyanobenzoate), and 4 equivalents of pyrrole (0.680, 9.80 mmoles) that had been freshly distilled over CaH\(_2\) in N\(_2\). Dry N\(_2\) was then bubbled through solution for 30 minutes. To the solution, BF\(_3\) etherate (0.680 mL) was added, which resulted in the solution color changing from light yellow to deep purple. After 1.5 h at room temperature, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.2 g) was added to the solution, which was stirred for another 45 min. Finally, triethylamine (0.4 mL) was added to the solution, and the solvent was removed in vacuo. The product was purified using column chromatography on 32-63 micron Selecto Scientific silica gel using CH\(_2\)Cl\(_2\) and hexanes. The desired porphyrin product strongly fluoresces under a black light, and purification was confirmed using H\(^1\) NMR.

The acid porphyrin molecules were synthesized by adding the ester porphyrin (50 mg) to a solution containing tetrahydrofuran (50 mL), H\(_2\)O (25 mL), and KOH (1.24 g). The solution was refluxed for 16 hours using a 110 °C oil bath. The reaction was cooled to room temperature, and HCl was added until the solution was mildly acidic. After the addition of minimal toluene to form 2 clear layers, the solution was washed with saturated NaHCO\(_3\) (50 mL) and H\(_2\)O (3 x 50 mL), dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The product was purified using column chromatography on 32-63 micron Selecto Scientific silica gel using CH\(_2\)Cl\(_2\) and ethyl acetate. The saponification reaction yield takes place in high yield, and the acid product
was easily separated from the ester using column chromatography. The product was confirmed using $^1$H NMR.

The resulting acid porphyrin (50 mg) was dissolved in CHCl$_3$ (60 mL) into which was added a solution of Zn(ac)$_2$∙2H$_2$O (0.20 g) in methanol (10 mL). The solution was refluxed for 2 h and cooled to room temperature. The solution was then washed with saturated NaHCO$_3$ in H$_2$O (3 x 50 mL), dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The product was purified using column chromatography on 32-63 micron Selecto Scientific silica gel using CH$_2$Cl$_2$ and ethyl acetate. The metalation reaction takes place in high yield, and if any unreacted product remains, the metalation reaction can easily be repeated. The product was confirmed using $^1$H NMR.
Figure 3.2: Synthesis of the three porphyrin molecules
3.3 Results and Discussion

3.3.1 Zinc Oxide Nanoparticles

Nanoparticles of a range of sizes were produced and characterized with ultraviolet visible absorption and transmission electron microscopy. The particle sizes and ultraviolet visible absorption were described in Chapter 1. The particles were calculated to be 2.8, 3.6, and 4.7 nm in diameter. TEM images of 4.7 nm ZnO particles are shown in Figure 3.3.

3.3.2 Optical Characterization

Shown in Figure 3.4 is the normalized absorbance and photoluminescence of these dyes. The ZnP and ZnCNP have similar absorptions and emissions. The ZnDTAP molecule’s λ max absorption at its Soret band is 9 nm higher in wavelength and broader than the other two dyes, and the absorption at its Q-bands are higher in wavelength than the other two dyes. The ZnDTAP molecule’s emission has a significantly different shape and is at higher in wavelength than different the other two dyes. The ZnDTAP has a fairly strong absorbance in the ultraviolet region that is most likely due to the ditolylaminophenyl groups.
Figure 3.3: Transmission electron microscope images of 4.7 nm ZnO nanoparticles.
Dye / $\lambda_{\text{max}}$ | Soret Band (nm) | Q Band (nm) | Emission (nm)
--- | --- | --- | ---
ZnDTAP | 433 | 562 and 605 | 622
ZnP | 424 | 559 and 597 | 603 and 657
ZnCNP | 424 | 557 and 599 | 607 and 657

**Figure 3.4:** Normalized ultraviolet visible absorption and photoluminescence for the three porphyrin dyes.
3.3.3 Electrochemistry

Electrochemistry was done to measure the ground state oxidation potentials of the dyes. Using the ultraviolet visible absorption and photoluminescence data for the dyes, the $E_{0-0}$ of the dyes was calculated. The $E_{0-0}$ was the average of the lowest energy absorption peak and the highest energy photoluminescence peak and represents the approximate difference in energy between the excited state and ground state of the dye. By subtracting the $E_{0-0}$ value from the oxidation potential of the dye, the excited state energy of the dye can be calculated, which is shown in Figure 3.5 for the three dyes. The dyes showed an increasing excited state potential with increasing electron donation from the groups connected to the porphyrin core.

Using the literature method for calculating nanoparticle size, the conduction band energies of the ZnO nanoparticles were estimated, which are also shown in Figure 3.5. After comparing the energies of the dyes and conduction band energies, all three dyes should be able to inject electrons from their excited state into all of the ZnO sizes used in this study.
Figure 3.5: The excited state energies of the dyes compared to the calculated conduction band energies of the ZnO nanoparticles.
3.3.4 Density Functional Theory Analysis

The porphyrin dye molecules were studied computationally using density functional theory to determine the electronic structure of the HOMO and LUMO of the molecules. This work was done in collaboration of Rajan Vatassery. Shown in Figure 3.6 to Figure 3.11 are the calculated HOMOs and LUMOs for the protonated form of the three porphyrin dyes that were studied. These images show the effect of the groups connected to the porphyrin core on the position of the HOMO and LUMO.

The ZnDTAP molecule has the strongest electron donating groups of the series connected to the porphyrin core. The HOMO is spread throughout the core and the ditolylamino groups. The LUMO however is spread over the core and the carboxyphenyl group. The ZnP molecule has a HOMO that is largely contained in the porphyrin core of the molecule. The LUMO is spread between the core and the carboxyphenyl group. The ZnCNP molecule has a HOMO that is spread throughout the molecule. Its LUMO is different from the other two molecules in that it has very little electron density on the carboxyphenyl group.

The molecular orbital structures of the porphyrin molecules are in agreement with the experimental observation of electron injection into a semiconducting nanoparticle. The carboxylic acid binding group has LUMO contribution increasing from ZnCNP, ZnP, to ZnDTAP. The more LUMO contribution on the carboxylic acid binding group observed computationally correlates with the results seen in steady state and time resolved photoluminescence experiments.
Figure 3.6: The calculated HOMO of ZnDTAP.
Figure 3.7: The calculated LUMO of ZnDTAP.
Figure 3.8: The calculated HOMO for ZnP.
**Figure 3.9:** The calculated LUMO of ZnP.
Figure 3.10: The calculated HOMO for ZnCNP.
Figure 3.11: The calculated LUMO for ZnCNP.
3.3.5 Photoluminescence Quenching Experiments

Electron transfer of photoexcited dyes into ZnO nanoparticles was investigated using steady-state photoluminescence and time correlated single photon counting. Steady-state photoluminescence is an important tool in studying electron transfer and quenching, but cannot determine the mechanism and electron transfer rates alone. Both Stern-Volmer quenching and Langmuir isotherm experiments were both done using steady-state photoluminescence.

Stern-Volmer experiments are done using a constant concentration of dye and varying the concentration of ZnO nanoparticles. Separate solutions are made for each measurement so that dilution is not an issue. Equation 1 is the form that Stern-Volmer used to fit the experimental data.

\[
\frac{I}{I_0} = 1 + K_{sv} [Q] \quad (1)
\]

The \( K_{sv} \) is the Stern-Volmer constant, and \([Q]\) is the concentration of the quencher, which was the concentration of ZnO in these experiments. The photoluminescence intensity is given by \( I \), and \( I_0 \) is the intensity without any quencher present. The constant \( K_{sv} \) is dependent on the type of quenching. Because porphyrin molecules bind to ZnO nanoparticles, the quenching is static.

Langmuir isotherm experiments are done using a constant concentration of quencher while varying concentrations of dye. Langmuir isotherms were designed to describe absorption of gases onto a surface, and the equation is based on assumptions that are valid for gas absorption. Although the assumptions of the Langmuir isotherm aren’t completely valid for the binding of acid dyes in solution, Langmuir isotherms have been
used for similar conditions successfully.\textsuperscript{191–193} Equation 2 is the Langmuir absorption equation.

\[
\theta = \frac{\text{Coverage}}{\text{Coverage}_{\text{max}}} = \frac{a[dye]}{1+a[dye]}
\]  

(2)

In Equation 2, $\theta$ is the fractional coverage, $[\text{dye}]$ is the equilibrium concentration of unbound dye, the coverage is the amount of dye absorbed to the surface, the $\text{coverage}_{\text{max}}$ is the maximum coverage fit from the data, and $a$ is the binding constant fit from the data. In processing the data, the equilibrium concentration of unbound dye must be adjusted for the portion of the dye that attached to the ZnO.

Time correlated single photon counting was used to investigate the injection rates of the dyes. Time correlated single photon counting is a time resolved photoluminescence measurement, which allows for an understanding of the photoluminescence decay rates of the dye alone and when bound to ZnO. In combination with steady-state photoluminescence measurements, time correlated single photon counting is important for understanding the quenching mechanism and the percentage of quenched dyes.

### 3.3.6 Steady State Quenching and Stern-Volmer Experiments

Stern-Volmer quenching experiments were done on all three dyes with 2.7 nm ZnO nanoparticles in methanol. The reported results were collected by exciting the dyes at the peak of their Soret bands, and the data from the Stern-Volmer experiments are shown in Figure 3.12. Similar data were also collected by exciting the dyes at their Q-Bands, but the data are not shown. All three dyes displayed a photoluminescence quench when ZnO nanoparticles were added in solution with the dyes. Both the ZnDTAP and ZnP dyes retained a consistent relative photoluminescence intensity curve while
quenching, meaning the photoluminescence curves are identical if normalized in intensity. In contrast, the ZnCNP relative photoluminescence intensity changed during quenching, and showed differences in photoluminescence curves if the data are normalized in intensity. This can be seen by examining the ZnCNP photoluminescence data shown in Figure 3.12. Before the addition of ZnO into the ZnCNP solutions, the 607 and 657 nm photoluminescence emission peaks have nearly identical intensities. At maximum quenching, the 607 emission peak has significantly lower intensity than the 657 nm emission peak. This change in relative photoluminescence intensity is likely due to interaction between dyes. The cyano groups are able to interact with the zinc metal in the porphyrin molecule, which affects the photoluminescence shape of the molecule.

The Stern-Volmer experiments displayed the result of changing ZnO nanoparticle concentration on the photoluminescence quenching on the dyes. On the Stern-Volmer plot, each of the dyes showed a linear increase in quenching factor with increasing ZnO nanoparticle concentrations at low ZnO nanoparticle concentrations, a peak in quenching factor at intermediate ZnO nanoparticle concentrations, and a decrease into a plateau of the quenching factor at the highest ZnO nanoparticle concentrations. This quenching behavior is different than expected for quenching based on binding. Several static quenching studies with a binding between a photoexcited dye and a nanoparticle quencher show a linear increase in quenching factor at low binding site concentration into a plateau at high concentration, and do not contain the peak at intermediate binding site concentration as seen in this study.\textsuperscript{194–198} This suggests that these porphyrin dyes undergo more than binding and quenching, and another mechanism is affecting quenching at intermediate ZnO nanoparticle concentrations.
It is likely that the peak in the quenching factor at intermediate ZnO nanoparticle concentration during the Stern-Volmer experiment for this set of experiments was in part due to a changing of the solvent environment of the dye, which can affect the absorption and emission of the dye. At intermediate concentrations of ZnO at the peak in quenching factor, there were an equal number of ZnO binding sites and dyes in solution, which leads to the majority of dyes being in close interaction with other dyes and therefore less solvent molecules.

In the ultraviolet visible absorption of the molecules shown in Figure 3.13, Figure 3.14, and Figure 3.15, there was a broadening effect on the Soret band for each of the dyes that reached its maxima near the ZnO concentration with the peak in quenching factor of the Stern-Volmer plot. At this point in the experiment, there were both a low percentage of unbound dyes and the number of dyes bound per nanoparticle was at its maximum.

At ZnO concentrations lower than the quenching factor peak, there was a large portion of the dye in solution that was unbound contributing to the photoluminescence and ultraviolet visible light absorption. At ZnO concentrations higher than the quenching factor peak, there was a low percentage of unbound dye but the number of dyes per nanoparticle was lower than at the quenching factor peak, and the ultraviolet visible absorption of the Soret band was less broad and lower in energy. This can be attributed to the bound dyes interacting more with solvent than dye molecules when compared to the quenching factor peak.

These data for quenching and the Stern-Volmer peak could potentially be explained by binding to Zn²⁺ ion as our group reasoned for another dye. However,
there are significant differences between the experimental results seen for these experiments and the experimental results that were reasoned with Zn\textsuperscript{2+} ion binding. In those results, there were not ultraviolet visible absorption changes upon binding and the low dye concentration portion of the Langmuir isotherm was not linear.

It is not possible from these data to fully determine the mechanism behind the ultraviolet visible absorption broadening and the Stern-Volmer quenching factor peak. Under these conditions, these observations may be due to dyes being more likely to inject electrons into ZnO, the quantum yield of photoluminescence may be decreased, or less light is being absorbed or the light was absorbed at a different position in the instrument due to the absorption decrease. It is also possible that two or more of these processes may be taking place during this experiment.

These experimental results strongly suggest that the Stern-Volmer quenching factor peak is caused by a light absorption decrease due to a broadening in the ultraviolet visible absorption data. The broadening in the ultraviolet visible absorption data is most likely caused by dye-dye interactions or the dye chemical environment containing less solvent. This conclusion is further supported by the experimental observation in ZnCNP which showed a change in the relative photoluminescence intensity curves for at intermediate ZnO nanoparticle concentrations.

The decrease in ultraviolet visible absorption causes there to be less photoluminescence due to both less light being absorbed and for the photoluminescence to occur at a different position in the cuvette inserted into the instrument because of the absorption decrease, which has been shown to lower the measured intensity due to instrumental and experimental limitations. Due to the absorption change being larger than
30% of the original absorption for each of the dyes, there was not a simple modification that could be done to correct for these difference.
Figure 3.12: Quenching and Stern-Volmer plots using 2.7 nm ZnO nanoparticles as quenchers for the three porphyrin dyes: (top) ZnDTAP, (middle) ZnP, and (bottom) ZnCNP. The photoluminescence intensity for all of the dyes decreases followed by a small recovery of intensity.
Figure 3.13: Ultraviolet visible absorption of the ZnDTAP dye during the Stern-Volmer experiment. The enlarged Soret region is shown at bottom. The Soret band broadens and shifts to lower in energy, and then shifts further lower in energy and sharpens. The progression of the Soret peak is indicated by the downward arrow followed by the upward arrow.
Figure 3.14: Ultraviolet visible absorption of the ZnP dye during the Stern-Volmer experiment. The enlarged Soret region is shown at bottom. The Soret band broadens and shifts to lower in energy, and then shifts further lower in energy and sharpens. The progression of the Soret peak is indicated by the downward arrow followed by the upward arrow.
Figure 3.15: Ultraviolet visible absorption of the ZnCNP dye during the Stern-Volmer experiment. The enlarged Soret region is shown at bottom. The Soret band broadens and shifts to lower in energy, and then shifts further lower in energy and sharpens. The progression of the Soret peak is indicated by the downward arrow followed by the upward arrow.
3.3.7 Langmuir Isotherms

Langmuir isotherm experiments were carried out on the ZnP dye with 2.8, 3.6, and 4.7 nm ZnO nanoparticles. Langmuir isotherm experiments were conducted using a constant concentration of ZnO nanoparticles and varying the amount of dye. For each data point and dye concentration on the Langmuir isotherm, the photoluminescence intensity was taken for both the dye by itself and a mixture of the dye with ZnO nanoparticles. The intensities were then compared to determine the amount of quenching.

Using the data obtained from time correlated single photon counting experiments, there was a correction done to the photoluminescence to determine the amount of dye that was bound. Because the rate of the dye alone and dye quenching were close to one another, even bound dyes would competitively photoluminescence or quench. It was calculated that the amount of dye that was bound was greater than the photoluminescence quench by 19% for 2.8 nm ZnO, 15% for 3.7 nm ZnO, and 13% for 4.9 nm ZnO. These values were determined by comparing the rates of injection and radiative decay. The dye by itself had a lifetime of 2.3 ns, and when bound to 2.8 nm ZnO nanoparticles, the injection lifetime was 369 ps. The lifetimes were determined by time resolved photoluminescence, which is discussed in the next section. Comparing the lifetimes of injection and radiative decay, it was determined an excited dye would still emit 19% of its original photoluminescence even with all dyes bound to ZnO nanoparticles due to the similar lifetimes of photoluminescence and electron injection.

Two values are fit using the Langmuir isotherm: the binding constant and the maximum coverage of the dye. Neither of these values was found to be dependent on the size of the nanoparticles. Using the maximum coverage of the dye, the surface area
calculated from nanoparticle diameter, and concentration of the nanoparticles, the surface area per dye was not found to be dependent on nanoparticle size the average value across all of the experiments was calculated to be $1.3 \pm 0.2 \text{ nm}^2$. The binding constant was also found to be independent of nanoparticle size and an average binding constant was calculated to be $7 \pm 3 \times 10^5 \text{ M}^{-1}$, which is similar to values that have been measured for other dyes containing carboxylic acid binding groups on metal oxides.$^{191-193}$
Figure 3.16: Langmuir isotherms for ZnP with a range of ZnO nanoparticle sizes. (top) The data fit separately for each size and (bottom) the average fit for all of the data.
3.3.8 Time Correlated Single Photon Counting

Time correlated single photon counting measurements were done using all the three dyes with a range of nanoparticle sizes. These data were taken in collaboration with Adam Huss and Tom Pundsack. Each of dyes had a different excited state potential and the conduction band energy of the nanoparticles increase with decreasing size. The measurements the dyes are shown in Figure 3.17, Figure 3.18, and Figure 3.19. The dyes had similar lifetimes without ZnO nanoparticles: 2.2 ns for ZnDTAP, 2.3 ns for ZnP, and 1.7 ns for ZnCNP, and both ZnDTAP and ZnP showed a significant difference between the decay rate without ZnO and when attached to ZnO.

The dye decay rate of ZnDTAP with any of the nanoparticle sizes was faster than the instrument could resolve. ZnCNP showed a similar decay with a range of nanoparticle sizes. However, ZnP showed a decay rate that was dependent on the size of the nanoparticle, and between the other two dyes in rate.

The lifetimes for the ZnP dye on ZnO nanoparticles was be determined by analyzing the data in Figure 3.19: 369 ps on 2.8 nm ZnO, 299 ps on 3.7 nm ZnO, 258 ps on 4.9 nm ZnO, and 245 ps on 5.4 nm ZnO. The analysis is described in previous work in collaboration with Adam Huss. This change in lifetime was due to an increase in the density of state the dye was able to inject into, which depended on the energy difference between the excited state potential of the dye and the conduction band of the ZnO nanoparticles. As the conduction band decreases in energy with increasing particle size, there is an increased density of state for electron injection from the porphyrin molecules and a faster injection lifetime.
It is likely that the other two dyes have decay rates dependent on the ZnO nanoparticle size that cannot be measured with this data. The ZnDTAP dye is faster than the instrument can measure on all of the nanoparticle sizes, so a difference could not be measured. The measurement on ZnCNP could have been complicated by dyes interacting with one another or the lifetime was too close to the dye alone lifetime to be determined with this experiment.
Figure 3.17: Time correlated single photon counting data for the three porphyrin dyes on ZnO nanoparticles
Figure 3.18: Time correlated single photon counting of the (top) ZnDTAP and (bottom) ZnCNP dyes with a range of nanoparticle sizes.
Figure 3.19: Time correlated single photon counting of the ZnP dye with a range of nanoparticle sizes. The decay rate was found to be dependent on the size of the ZnO nanoparticle.
3.4 Conclusions

Three porphyrin dyes were synthesized and attached to ZnO nanoparticle between 2.7 and 5.4 nm in diameter, which were small enough to be quantum confined. The dyes were all investigated computationally to determine their HOMO and LUMO characteristics. In steady state photoluminescence experiments, the dyes were found to all quench on the ZnO nanoparticles. ZnDTAP showed the largest quenching, ZnP less quenching, and ZnCNP showed the smallest amount of quenching. Using time correlated single photon counting, ZnDTAP have the fastest decay rate when quenched with ZnO nanoparticles, ZnP had slower injection, and ZnCNP had the slowest injection. Also, the ZnP dye showed an injection rate that was dependent on the size of the ZnO nanoparticle used. The dyes showed decay rates that increased with increasing energy between the nanoparticle conduction band and excited state potential of the dye.

Langmuir isotherms were done using the ZnP dye with 2.8, 3.6, and 4.8 nm ZnO nanoparticles. The binding constant of the dye was not dependent on the nanoparticle size, and found to be $7 \pm 3 \times 10^5 \text{M}^{-1}$. Using the nanoparticle size and fit maximum coverage, the surface area of the dye was calculated to be $1.3 \pm 0.2 \text{nm}^2$.
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