SYNTHESIS OF ZINC TELLURIDE/CADMIUM SELENIDE/CADMIUM SULFIDE QUANTUM DOT HETEROSTRUCTURES FOR USE IN BIOLOGICAL APPLICATIONS

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ABSTRACT

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This study investigates the synthesis of charge-separating quantum dots specifically engineered to be used as voltage sensitive probes in mapping of neuronal networks. ZnTe/CdSe/CdS core/shell/shell is the proposed system. The dots spatially separate charges and show the Stark effect under applied voltages, making them perfect for use as voltage sensitive probes. Synthesis techniques and characterization methods are given.
This work is dedicated to my mother and father, for seeing my potential when others said I had none. I love you both very much
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CHAPTER 1: GENERAL INTRODUCTION

Quantum Dots

Quantum dots (QDs) have recently been the focus of intense study due to the broad scope of their possible applications, including photocatalysts\(^1\)\(^-\)\(^5\), photovoltaics\(^6\)\(^-\)\(^20\), light emitting devices\(^29\)\(^-\)\(^37\), and transistors\(^38\)\(^-\)\(^43\), and their unique optoelectronic and functional characteristics, such as size tunable band gaps, strong emission, thermal and chemical stability, and the ability to change solubility via a change in surface ligands. QDs are semiconductor nanocrystals that confine excitons, or separated electron-hole pairs, in three dimensions and are surrounded by a layer of ligands, molecules that passivate the surface states of the QD and control its solubility. As the size of the material in question decreases from a bulk semiconductor to an object with one or more dimensions on the order of the exciton’s Bohr radius, the particles begin to “feel” the boundary of the surface and the band edge states of the bulk material become discrete states. As the size of the QD decreases, the separated charges are kept close together, increasing their Coulombic interactions. This translates to a blue-shift in the emission from the bulk material as the QD gets smaller.

Nanocrystal Heterostructures

By growing a shell onto a nanocrystal of a material, chosen such that the band gap of the core material is completely contained inside of the band gap of the shell material, a potential barrier can be placed between the exciton and the surface states of the nanocrystal, thereby confining the electron and hole wave functions to the volume of the core and enhancing the emission of the crystal. These heterostructures are known as type I nanocrystals. If, instead, a shell is grown of a different material, chosen such that the lowest
unoccupied molecular orbital (LUMO) of the shell material resides inside the band gap of the core material and the highest occupied molecular orbital (HOMO) of the shell material sits below that of the core material, then promoted electrons will move to the shell and holes will be confined to the core. These structures are known as type II nanocrystals. In type II structures, increasing the size of the shell can reduce the rate of radiative recombination of the exciton and, thus, decrease the overlap of the electron and hole wave functions. Even with shells that confine one or both charges to the core, tunneling events can occur. Therefore, it is of vital importance that the energetics of the entire system, including the surface ligands, be chosen to achieve the desired functionality of the system. Differences between type II and I systems can be seen more clearly in figure 1.
Fig. 1. Schematic representation of energy level alignments in (a) type I and (b) type II QD heterostructures. The main consequence of each type of system is indicated and common examples are listed.

- Heightened emission
- PbS/CdS, CdSe/CdS (large CdSe)

- Spatial separation of charges
- ZnSe/CdSe, CdSe/CdS (small CdSe)
The growth mechanism of the shell, in addition to the relative energy levels of the two materials in question, is important in determining the properties of the end product of a string of syntheses. The two methods used most often for colloidal QDs are ion exchange and successive ionic layer adsorption and reaction (SILAR). In either case, solutions of precursors are made and injected into a hot reaction solution. The heat breaks the precursors down into constituent monomers and these monomers will become the shell.

For ion exchange reactions, a high concentration precursor of one element is added to QDs of a different, usually binary, material. The monomers from the precursor “dig” into the lattice of the QDs and replace one type of atom in the lattice. By controlling the temperature, the penetration depth of these monomers can be controlled to create a core/shell system with the desired core diameter and shell thickness. The shell growth of these structures is marked by two distinct optical phenomena. One, a blue-shift in the absorption peak of the QDs, as the core diameter shrinks from the ion exchange. Two, a red-shift in photoluminescence, for type II systems, or an increase in photoluminescence intensity and a blue-shift in photoluminescence, for type I systems, from the growth of the shell. The increase in emission intensity for type I systems is due to a lowered probability of charges moving to surface trap states, since those states are now occupied by the shell. The red-shift in photoluminescence for type II systems is attributed to radiative recombination across the material interface, which is of lower energy than emission across the band gap of either individual material.

For SILAR reactions two separate precursor solutions are injected into a heated solution of QD cores. One of the monomers from the precursor solution will bond with the surface states of the core to form a layer of that element on top of the QD. Next, the
monomer from the second precursor attaches itself to the open states on the surface of that layer. The monomers then layer themselves on top of one another in alternating layers, until the concentration of monomers becomes too low to continue shell growth or the temperature is decreased until the reaction is quenched. The shell growth from SILAR reactions is marked by either a red-shift in the photoluminescence, for type II systems, or an increase in photoluminescence intensity, for type I systems, due, again, to radiative recombination across the interface or a lowered probability of charges reaching surface trap states, respectively.

The Quantum Confined Stark Effect

One interesting optoelectronic property of QDs is the quantum confined Stark effect, a phenomenon that is seen in the photoluminescence of spatially separated excitons under an external applied voltage. Due to their opposite charges, a voltage will push holes in one direction and electrons in the opposite direction, thereby reducing their Coulombic interaction and slightly red-shifting their emission upon recombination\textsuperscript{44, 45, 46}. Figure 2 shows the change in energy level alignment due to this process. Type II QD nanorods, which exhibit quantum confinement in two dimensions, are ideal for applications involving the Stark effect. The unique morphology found in these rods allows them to spatially separate charges into the distinct domains of a type II system, while the elongated axis of the rod allows for further spatial separation than core/shell structures comprised of similar materials. In spite of these advantages, implementation of nanorods may be more difficult due to the rods intrinsic lack of symmetry and the possibility of the preferred axis of the nanorod requiring a specific orientation when applied to a substrate. Using a more symmetric type II core/shell structure, charges can be spatially separated enough to see a
Stark shift, while avoiding the potential obstacles related to attaching a nanocrystal with a preferred orientation to a substrate.

**Fig. 2.** Energy level diagrams for ZnSe/CdS rods under application of (a) zero voltage and (b) a nonzero voltage. Rods are shown here to emphasize the effects dependence on the spatial separation between charges.

Bioimaging

Due to the strict constraints that must be met, producing an effective biolabel is an excellent opportunity to show the potential versatility of QD applications. Bioimaging requires emission in a specific wavelength range, around 900 nm (to be seen through the skin), solubility and stability in water, a measurable reaction to stimuli present in the body to be studied, and materials that will not harm the body. Current biolabeling approaches
include electrophysiological methods\textsuperscript{47,48}, organic fluorophores\textsuperscript{49}, and ion-sensitive probes\textsuperscript{50,51}. These approaches have distinct shortcomings, though, such as poor temporal resolution, spatial resolution too poor for use on single cells, and an inability to show the specific location of the cell being studied. Very little research has been done to incorporate QDs into biolabeling schemes, in spite of the niche that could successfully be filled by this technology.

Goal

The goal of this study was to synthesize a QD heterostructure that can act as a voltage sensitive probe in biological applications, such as mapping the paths of electrical impulses through neurons in the brain, while overcoming some of the limitations of the current biolabeling approaches. A QD system with carefully selected energetics could create an effective probe of this type. The proposed architechtuure, ZnTe/CdSe/CdS core/shell/shell, has the ability to spatially separate photoinduced holes and electrons into the ZnTe and CdSe domains of the QD, respectively. This opens up the prospect of putting the system under an applied voltage to measure a Stark shift in the emission. In addition, the surfaces of these QDs can be passivated with hydrophilic ligands without the worry of holes tunneling from the core domain to the ligand moiety, as the HOMO of the ligand sits above the HOMO of the ZnTe core. The electrons face a type II interface at the ZnTe/CdSe boundary and a type I interface at the CdSe/CdS boundary and are, thus, confined to the CdSe domain. Tuning the energetics in this way forces radiative recombination across the ZnTe/CdSe interface, which is associated with redder emission. Figure 3a demonstrates the energy level alignment of the nanocrystal. This system can also be made to emit, provided a thick shell of CdS is grown, in the red-to-near-infrared region of the electromagnetic
spectrum. This is ideal for bioimaging due to the constraint of visibility of the photoluminescence and the expense of mid- and far-infrared emission detection systems. An end goal for this project is to map neuronal pathways to further understand the electronics at work in the brain and to search for abnormalities in these pathways that may be related to neurodegenerative diseases, such as Alzheimer’s, Parkinson’s, and Huntington’s diseases. Dr. Alex Savtchenko, visiting researcher at the Sanford Burnham Medical Research Center and Collaborator on this project, will perform the portion of the study that maps the neuronal pathways and deals with any manipulation of neurons or living cells.
Fig. 3. (a) A schematic representation of the proposed ZnTe/CdSe/CdS QD structure with energy level alignments and key properties. The ligand is 11-mercaptoundecanoic acid (MUA). TEM images of (b) ZnTe cores and (c) a ZnTe/CdSe core shell structure.

- High fluorescence QY in water
- Photoinduced charge separation
CHAPTER 2: EXPERIMENTAL PROCEDURE

Chemicals

Sulfur (99.999%, Acros), 1-octadecene (ODE, tech., 90%, Aldrich), cadmium oxide (CdO, 99.99%, Aldrich), oleic acid (OA, tech., 90%, Aldrich), tri-n-octylphosphine (TOP, 97%, Strem), 11-mercaptoundecanoic acid (MUA, 95%, Aldrich), tellurium powder (Te, -200 mesh, Acros), diethyl zinc (Et₂Zn, 95%, 10% wt. in hexane, Aldrich), methanol (anhydrous, 99.8%, Aldrich), ethanol (anhydrous, 95%, Aldrich), and chloroform (anhydrous, 99%, Sigma) were used as purchased. All reactions were performed under argon atmosphere using the standard air free Schlenk technique unless otherwise stated. CdSe and CdS shells were synthesized using a seeded-type approach by introducing small-diameter seed nanocrystals into the reaction mixture for nucleating the growth of CdSe and CdS extensions.

Characterization

UV-vis absorption and photoluminescence spectra were recorded using CARY 50 scan spectrophotometer, and Jobin Yvon Fluorolog FL3-11 photoluminescence spectrophotometer. High-resolution transmission electron microscopy measurements were carried out using JEOL 311UHR operated at 300 kV. Specimens were prepared by depositing a drop of nanoparticle solution in an organic solvent onto a carbon-coated copper grid and letting it dry in air.

Synthesis of ZnTe QDs

QDs were synthesized from an adapted version of a procedure described in reference 52. 0.026 g of Te powder was mixed with 1.0 mL TOP in a flask (precursor flask) and degassed for 1 hour at 120° C. The mixture was subsequently placed under Ar flow and sonicated at room temperature for ~30 minutes to achieve an optically clear solution. Meanwhile, a flask (the reaction flask) containing 0.089 mL OA and 3.8 mL ODE was
degassed for 1 hour at 120° C and placed under Ar flow. This flask was then raised to 260° C to prepare for injection. After sonication of the Te solution, 1.93 mL of Et₂Zn solution was injected into the Te precursor flask and allowed to mix for ten seconds. The entire Te precursor solution, at room temperature, was then injected into the reaction flask and the solution was allowed to react at 260° C for ~4 minutes or until any aggregate forms. Removing the reaction flask from the heating mantle and allowing it to cool in air quenched the reaction. The end solution was a rusty orange color and very cloudy. Once the temperature of the reaction flask dropped below 60° C, 1.0 mL of anhydrous chloroform and 12.0 mL of anhydrous ethanol were added to the reaction flask and the entire solution was split into two vials. The vials were topped off with anhydrous ethanol and centrifuged at 5,400 RPM for 15 minutes to precipitate the QDs. The liquid was poured off and the precipitate was redissolved in 8.0 mL of anhydrous chloroform and stored in a glass vial topped off with anhydrous chloroform to leave as little room for air as possible.

Synthesis of CdSe Shell Onto ZnTe QDs

To separate photoinduced charges and enhance the stability of the ZnTe cores, a CdSe shell was grown according to a modified version of a procedure described in reference 53. A Cd precursor solution was prepared by adding 0.02 g CdO, 0.3 mL OA, and 3.0 mL ODE in a flask, while adding 0.01 g Se and 3.0 mL TOP to a separate flask prepared a Se precursor solution. The reaction flask was prepared by adding 1.5 g ODA and 6.3 mL ODE, and each flask was degassed for 1 hour at 120° C and was subsequently placed under Ar flow. The Cd precursor solution was then heated to ~290° C, until the solution became optically clear and colorless, and then taken off the heating mantle and left to cool to room temperature. Meanwhile, the Se precursor solution was sonicated until all the Se powder
had dissolved (~30 minutes). The Cd and Se precursor solutions were then mixed and allowed to mix. During this time, about half of the ZnTe QDs, in chloroform, from the previous step were added to the reaction flask and heated to 240° C, allowing the chloroform to boil off. 0.1 mL of the precursor solution was added to the reaction flask every 10 minutes, with the first injection happening immediately upon the reaction flask reaching 240° C, or if any aggregate is seen forming in the reaction flask. The emission was checked every 10 minutes, starting 5 minutes after the initial injection, until the emission peak coincided with the desired wavelength. For the QDs used in this experiment, the reaction was stopped when the emission peak reached ~850 nm (~35 minutes). Removing the flask from the heating mantle and placing it in a water bath quenched the reaction. Once the reaction flask dropped below 60° C, 12.0 mL of ethanol was added and the solution was split into two vials. Each vial was topped off with ethanol and the vials were centrifuged at 5,400 RPM for 15 minutes to precipitate the QDs. The liquid was poured off and the precipitate was redissolved in 1.0 mL chloroform, and the vials were topped off with ethanol and centrifuged again. The precipitate was again redissolved in chloroform and stored in a glass vial.

**Synthesis of CdS Shell Onto ZnTe/CdSe Nanocrystals**

In order to create a potential barrier between the photoinduced charges and the ligand moiety, a thin CdS shell was grown onto the ZnTe/CdSe nanocrystals from the previous step via a modified version of a procedure described in reference 4. A Cd precursor solution was prepared by adding 0.02 g CdO, 0.3 mL OA, and 3.0 mL ODE in a flask and a S precursor solution was prepared by mixing 0.004 g S and 3.0 mL ODE in a separate flask. Both solutions were placed under Ar flow. The reaction flask was prepared
by combining 1.5 g ODA and 6.3 mL ODE and degassing the solution at 120° C for 1 hour, at which point it was placed under Ar flow. The Cd precursor solution was heated to ~290° C until the solution became optically clear and colorless. Meanwhile, the S precursor solution was heated to 200° C until optically clear and colorless. Both flasks were removed from their respective heating mantles and allowed to cool, in air, to room temperature. The two precursor solutions were then mixed and left to stir. During this time, about half of the ZnTe/CdSe, in chloroform, from the previous step were added to the reaction flask and the solution was heated to 240° C, allowing the chloroform to boil off. 0.07 mL of the precursor solution was added to the reaction flask immediately when the reaction flask reached 240° C. The emission was checked every 5 minutes, starting 2 minutes after the initial injection, until the emission peak shifted to the desired wavelength. For the nanocrystals used in this experiment, the reaction was stopped when the emission peak reached ~900 nm, which corresponded to ~10 minutes of reaction time. Removing the flask from the heating mantle and placing it in a water bath quenched the reaction. Once the reaction flask dropped below 60° C, 12.0 mL of methanol was added and the solution was split into two vials. Each vial was topped off with methanol and the vials were centrifuged at 5,400 RPM for 15 minutes to precipitate the nanocrystals. The liquid was poured off and the precipitate was redissolved in 1.0 mL chloroform and the vials were topped off with methanol and centrifuged again. The precipitate was again redissolved in chloroform and stored in a glass vial.

Large Yield Synthesis of ZnTe QDs

A modified procedure from the one listed above was used to produce large yields, typically ~20 times greater, of ZnTe than the procedure discussed above. The drawback of
this procedure was that the size of the nanocrystals produced was typically smaller than could be produced by the original procedure. 0.056 g of Te powder was mixed with 2 mL TOP in a flask (precursor flask) and degassed for 1 hour at 120° C. It was subsequently placed under Ar flow and sonicated at room temperature for ~30 minutes to get an optically clear solution. Meanwhile, a flask (reaction flask) containing 3.5 mL OA and 5.0 mL ODE was degassed for 1 hour at 120° C and placed under Ar flow. This flask was then raised to 280° C to prepare for injection. After sonication of the Te solution, 4.0 mL of Et₂Zn solution was injected into the precursor flask and allowed to stir for ten seconds. The entire precursor solution, at room temperature, was then injected into the reaction flask and the solution was allowed to react at 280° C for 1 minute. The reaction flask was immediately removed from the heating mantle after 1 minute and was allowed to cool in air, quenching the reaction. The end solution was a rusty orange color and very cloudy. Once the temperature of the reaction flask dropped below 60° C, 1.0 mL of anhydrous chloroform and 12.0 mL of anhydrous ethanol were added to the reaction flask and the entire solution was split into two vials. The vials were topped off with anhydrous ethanol and centrifuged at 5,400 RPM for 15 minutes to precipitate the nanocrystals. The liquid was poured off and the precipitate was redissolved in 8.0 mL of anhydrous chloroform and stored in a glass vial topped off with anhydrous chloroform to leave as little room for air as possible.

**Single-Flask Growth of CdSe/ CdS Shells Onto ZnTe QDs**

To expedite the synthesis process, CdSe and CdS shells were grown using a single-flask synthesis that switched from CdSe precursors to CdS precursors once the growth of the CdSe shell had stopped. A Cd precursor solution was prepared by adding 0.04 g CdO,
.6 mL OA, and 6.0 mL ODE in a 3 neck flask, a Se precursor solution was prepared by adding 0.01 g Se and 3.0 mL TOP in another flask, and, in a third flask, the reaction mixture was prepared by adding 1.5 g ODA and 6.3 mL ODE. All three of these flasks were degassed for 1 hour at 120° C and then placed under Ar flow. Meanwhile, a S precursor solution was prepared by adding 0.004 g S and 3.0 mL ODE in a final flask. The Cd precursor solution was then heated to ~290° C, until the solution became optically clear and colorless, and then taken off the heating mantle and left to cool to room temperature. Meanwhile, the S precursor solution was heated to 200° C until optically clear and colorless and left to cool while the Se precursor solution was sonicated until all the Se powder had dissolved (~30 minutes). Half of the Cd precursor was added to the Se solution and the other half was added to the S solution. The new precursor solutions were left to mix while about half of the ZnTe from the previous synthesis was added to the reaction flask and heated to 240° C, letting all chloroform boil off. At 240° C, 0.1 mL of the Se precursor solution was added to the reaction flask, with the temperature set at 240° C, every 10 minutes, with the first injection happening immediately upon the reaction flask reaching 240° C, or if any aggregate is seen forming in the reaction flask. The emission was checked every 10 minutes, starting at 5 minutes after the initial injection, until the emission peak coincided with ~30 nm less than the desired emission for ZnTe/CdSe, to allow the reaction to use up all precursor left in the flask without overgrowing. For the QDs used in this experiment, the reaction was stopped when the emission peak reached ~820 nm (~30 minutes). Once the CdSe shell has stopped growing, 0.07 mL of the S precursor solution was added to the reaction flask ~10 minutes after the final Se precursor injection. The emission was checked every 5 minutes, starting 2 minutes after the initial injection, until the emission peak
shifted to the desired wavelength. For the nanocrystals used in this experiment, the reaction was stopped when the emission peak reached ~900 nm, which corresponded to ~10 minutes of reaction time. Removing the flask from the heating mantle and placing it in a water bath quenched the reaction. Once the reaction flask dropped below 60° C, 12.0 mL of methanol was added and the solution was split into two vials. Each vial was topped off with methanol and the vials were centrifuged at 5,400 RPM for 15 minutes to precipitate the nanocrystals. The liquid was poured off and the precipitate was redissolved in 1.0 mL chloroform and the vials were topped off with methanol and centrifuged again. The precipitate was again redissolved in chloroform and stored in a glass vial.

Ligand Exchange to MUA

To biofunctionalize, or optimize the system for use in living tissue, hydrophobic ligands on the ZnTe/CdSe/CdS nanocrystals were exchanged with the hydrophilic ligand MUA using a procedure reported in reference 54. The solution of nanocrystals, in 10-12 mL of chloroform, was mixed with 10.0 mg of MUA. Next, 4 mL of a KOH solution, prepared by dissolving 0.1 g KOH in 20.0 mL of triple-distilled water, was added to the nanocrystal solution and shaken vigorously until the nanocrystals were transferred to the aqueous phase. The phases were then separated with a syringe and the aqueous phase was treated again with 2.0 mL of the aqueous KOH solution. MUA capped nanocrystals were then precipitated by adding 10.0 mL of methanol and centrifuging at 5,400 RPM for 15 minutes, the precipitate was redissolved in ultrapure water.

Measuring Stark Shifts in ZnTe/CdSe/CdS Nanocrystals

Stark shift measurements were made using a homemade apparatus, shown in figure 4, to hold a solution of QDs and apply a voltage in front of a photoluminescence detector.
Two slides of indium tin oxide (ITO) coated glass were clamped together using teflon tape on each end to seal the sides, preventing the liquid from escaping, and space the slides. The space between the slides was 180 μm and the liquid was held in place by the capillary action of the two slides. The apparatus was then placed in front of a photoluminescence detector and put under UV light. The apparatus was filled with the nanocrystal solution and the emission was taken at zero V. Emission spectra were then taken with voltage applied, with a Hewlett Packard 6561A DC power supply, in 50V increments, with the apparatus being refilled between each data collection, up to 300V total.

Fig. 4. (a) Schematic representation of Stark effect measurement system and photos of the actual apparatus from (b) the front and (c) top views.
CHAPTER 3: RESULTS

TEM RESULTS

Nanocrystals were formed from a series of seeded growth syntheses, described in detail in chapter 2, which began with formation of ZnTe cores encased in different sized shells grown onto their surfaces via the SILAR method. The ZnTe cores synthesized were roughly spherical with an average diameter of 3.76 nm and a standard deviation of 0.47 nm. Large CdSe shells were subsequently grown onto the ZnTe cores to create a type II interface between the core and shell domains and promote spatial separation of photoinduced charges. Although the CdSe cores began as spherical shapes, mimicking the shape of the core structure, continued growth of the CdSe shell resulted in a roughly pyramidal prism, most likely due to lattice mismatches at the interface of ZnTe and CdSe propagating into the overall shape of the nanocrystal. The change in shape was also found in ZnTe/ZnSe core/shell structures in reference 52, and may be a common phenomenon for ZnTe seeded nanoheterostructures. CdS shells grown onto these pyramidal structures kept this shape for the most part through the final syntheses. The final structures had an average size, measured from one tip of the prism to the flat side opposite it, of 8.78 nm with a standard deviation of 1.08 nm.
Fig. 5. A series of TEM images spanning the growth of the entire ZnTe/CdSe/CdS nanocrystals. (a) ZnTe QDs. (b) ZnTe QDs with a thin shell of CdSe grown. (c) ZnTe QDs with a thick shell of CdSe grown. (d) ZnTe with a thick shell of CdSe and a thin shell of CdS grown.

Fig. 6. Close up TEM image of a ZnTe QD with a large CdSe shell. The pyramidally prismatic shape can easily be seen and reflected in the lattice orientation.
ABSORBANCE RESULTS

The absorbance of ZnTe cores showed a high absorbance toward the UV edge of the visible spectrum with indistinct features at ~ 350 nm and ~ 550 nm, as seen in figure 7a. The rise in absorbance toward the UV edge is common to nanocrystals, since photons of all energies above the band gap energy of the materials can produce excitons. The 350 nm peak was assumed to be due to limitations of the detector, while the 550 nm peak was thought to be the representative absorbance feature of ZnTe. Absorbance spectra of the samples across the shell growth showed a general trend of a drop in absorbance and a broadening of spectral features as the shell was grown. These features can be seen in fig. 7b. The drop in absorbance would most likely be attributed to the increase in solubility of the samples from the core stage to the core/shell stage. The shell growth procedure turned the highly insoluble ZnTe cores, which were visible cloudy in solution and mostly opaque, into readily soluble ZnTe/CdSe core shells, which were optically clear in solution. These cores would stay dissolved for about a week. This issue was probably caused by an incomplete attachment of ligands to the surface of ZnTe QDs, resulting in poor solubility. The broadening of spectral features in the absorbance of ZnTe during shell growth was shown in reference 52 and was attributed to the decreased wave function overlap associated with type II QD systems.
Fig. 7. Absorbance spectra of (a) ZnTe and (b) ZnTe/CdSe and ZnTe/CdSe/CdS throughout the visible range. All samples were in solution in chloroform.
PHOTOLUMINESCENCE RESULTS

Photoluminescence spectra of the heterostructures, which are shown in figure 8, during the growth of CdSe and CdS shells show the peak emission shifting continuously to redder wavelengths as time passes. This red-shift is indicative of shell growth of a type II system through a SILAR reaction because the size of the entire nanocrystal grows and the coupling energy between the separated charges decreases as the overlap of their wave functions shrink. The emission shift at the onset of shell growth is typically quite fast, as the nanoparticles are smaller, and begins around 650 nm. As the shells grow and the nanocrystals become larger, it takes more shell material to grow subsequent layers. Since the injections of precursor solutions are the same concentration and amount in each injection, the shell growth will slow with increasing nanocrystal size. The growth of the CdS shell onto the nanocrystal is also done with an injection of similar concentration and amount, so it’s growth continued at roughly the same rate as the CdSe shell would have, if allowed to continue.

Once the CdS shell was grown, and the ligands were switched to the hydrophilic ligand MUA, the QDs were dissolved in ultrapure water. The photoluminescence was checked again to detect any differences between the emission of nanocrystals, with hydrophobic ligands that are dispersed in chloroform and the same nanocrystals with hydrophilic ligands dispersed in an aqueous solution. As shown in figure 9, the intensity of emission of the nanocrystals was increased when dissolved in water. This increase in the emission intensity is to be expected, as the new ligand has a HOMO level that sits above the HOMO level of ZnTe. This makes a hole tunneling out to the ligand energetically
unfavorable, which increases the probability of radiative recombination of photoinduced excitons.

As a point of interest, ZnTe cores without a shell show no photoluminescence whatsoever. The growth of a small shell results in very strong emission from the QDs, due in part to the shell passivating the surface trap states associated with the incomplete ligand attachment mentioned in the absorbance section. With these states occupied, the separated charges are free to radiatively recombine. The more complete ligand attachment of the shell syntheses ensures that this problem is not pervasive after the growth of the CdSe and CdS shells.
FIG. 8. Normalized emission spectra for ZnTe QDs through the growth of CdSe and CdS shells. The case shell was grown for 35 minutes, at which point the CdS shell was grown for 1.0.

Emission during growth of CdSe and CdS shells onto ZnTe
Hydrophobic ligands in ultrapure water.

Fig. 4. Emission spectra for fully Brown-ZnTe/CdSe/CdS QDs with hydrophobic ligands in chlороform and with
STARK SHIFT RESULTS

ZnTe/CdSe/CdS core/shell/shell structures were tested for photoluminescence shifts due to the Stark effect by a procedure outlined in chapter 2. The main obstacle of making these measurements was the sinusoidal nature of the emission spectrum. The emission had periodic local maxima and minima along its main peak, which can be seen in figures 8 and 9, which made the true peaks of the spectra difficult to discern. This effect was originally believed to be due to some interference, at long wavelengths, in the fiber optic cables of the photoluminescence detector, but further study of shorter wavelength samples shows this is most likely not the case, and that this phenomenon is intrinsic to the material. Regardless of the data’s lack of a sharp, well-defined, peak, it was clear, from inspection, that the emission peak had shifted the expected few nanometers. To see this more clearly, the peaks were fit with 5th degree polynomials and the fits were normalized to do away with any visual uncertainty due to the differences in intensity at the emission peaks. The structures showed a Stark shift of ~3 nm when comparing the emission peak at zero V and the emission peak at 300V. An unfortunate side effect of doing these measurements is that the emission intensity shrinks with growing voltage, since the applied voltage separates the charges and lowers the chance of radiative recombination in the core domain. This drop in photoluminescence is irreversible due to an unknown effect.
300V

Fig. 10. Pl spectrum showing characteristic Stark shift between 0V and 300V.
CHAPTER 4: DISCUSSION

This chapter will begin with a brief discussion of pitfalls to avoid during the steps required for the various syntheses and how these problems can affect the end products. By far the most difficult aspect of this study was getting the synthesis to work correctly and reproducibly. Problems during the synthetic steps ranged from hole injection into the hydrophilic ligand, caused by ZnTe cores that were fabricated too small, to problems with aggregation during syntheses. Once these problems were remedied, however, the products of the syntheses were quite reliable and reproducible. Efforts began with a synthesis that was a scaled up ZnTe procedure that garnered great yields, ~20 times more QDs than the method it was derived from, but the procedure called for a high temperature and quick reaction time. The reaction time had to be short in this procedure, as the high temperature would cause the crystals to aggregate if the reaction was allowed to run longer than about a minute. The most prominent effect of this method was that the ZnTe cores were growing quite small and had correspondingly large band gaps. This wouldn’t manifest itself until the QDs were switched to the hydrophilic ligands, but these small ZnTe dots had a HOMO level below that of the ligand. When the ligands were switched to MUA, the photoluminescence would be completely quenched, due to holes running out to the HOMO of the ligand. To remedy this, a low temperature synthesis that offered the dots more time to grow was used. The second consequence of the high temperature, low-reaction time, method was a number of defects in the materials. Generally speaking, QDs synthesized from longer reactions form with a smaller number of lattice defects and trap states. These large yield batches would contain ~20 times more QDs than the low temperature procedure and still had weaker emission than dots, diluted by the same amount, from the low temperature
procedure. Shell growths saw the same kind of complications from high temperatures. ZnTe cores are very unstable and would often aggregate before the shell precursors could be added to the reaction if the temperature rose too quickly. If precursor materials were added quickly, the QDs that had not aggregated could be salvaged and then have shells grown on them but these were generally of much lower quality than properly synthesized core/shells.

The second major hurdle in this study was the aforementioned sinusoidal behavior of the emission peaks. The spectra were checked against spectra of CdSe dots at similar wavelengths with sharp emission peaks. The CdSe dots never showed this behavior on their peaks, even at wavelengths that matched those where ZnTe dots had shown the behavior. This evidence shows quite clearly that this effect is an intrinsic property of the material. Investigating what causes these local peaks would be an interesting avenue of future study in this area, as this implies that the sample has a size distribution that is periodic, and minimizing the effect of these peaks will be necessary for making measurements of the intended type in biological systems quickly and efficiently.

In spite of these setbacks, the final product of this research worked quite well. The dots not only maintained their photoluminescence intensity in water, but the intensity was actually enhanced, as can be observed from fig. 9. The emission shifts due to the Stark effect were also larger than expected. Core/shell structures usually exhibit Stark shifts around 1 nm, while core/shell/rod structures generally shift 4-5 nm. ZnTe/CdSe/CdS synthesized in this study were in between these two common values, at ~3 nm, due to the unique morphology of the dots after the shells were grown. The pyramidally prismatic shape of the dots offered extensions where the excited charges could become further spatially
separated than those in a corresponding dot that was spherically symmetric, but less so than in a nanorod structure. This shift is, however, enough to be easily visible with minimal data manipulation. The shifts were due to voltages applied to the nanocrystals, as would be found in neurons passing electrical signals through the body. The shifts took place in the proper range of the electromagnetic spectrum to pass through skin and thus be biologically viable, and were, according to the Stark shift data, voltage sensitive. The dots were found to be non-toxic when attached to the surface of living tissue cells by a collaborating researcher, and are extremely water-soluble. The ZnTe cores are quite unstable when exposed to air, and even degrade in chloroform in under a week. After the growth of the CdSe shell, however, ZnTe dots retain their photoluminescence for multiple weeks or longer. In this case, the highly stable shell materials are protecting the unstable core material from rapid oxidation.

The future of this research bifurcates at this point, now that the materials have been shown to work as intended, into optimization of the biofunctionality of the dots and study of the intrinsic properties of the dots themselves. One avenue for future research is the effect of morphology of the dots on both the Stark shift incurred under applied voltage and their ability to attach to cell walls. Morphology is a very influential characteristic in QDs, and studying the differences among the properties spherical dots, pyramidal dots, and rod structures would be a worthwhile pursuit. In addition, there is an issue with the solubility of the dots with MUA as a ligand. The dots appear to be too soluble in water; they can be individually placed onto cells, but do not naturally attach themselves from aqueous media onto cells. This is essential for mapping the neuronal networks of animals in vivo, as the dots would have to be injected into the bloodstream and be selectively deposited on
neuron walls. The proposed solution to this is to use a mixture of ligands to passivate the dots; some that were hydrophilic and allowed them to be carried in aqueous media, and some that were hydrophobic and could attach themselves to cell walls. The other direction to take the research would be into optimization of the dots themselves, independent of the biological constraints. The synthesis of ZnTe cores is still bothersome at this point, as it produces dots that are not soluble or photoluminescent and can easily aggregate during shell growth procedures. The problem could potentially lie in ligands not completely passivating the surface states of the dots. Some work on synthesizing dots with better-passivated surfaces would be worthwhile, as well as study into the local minima and maxima associated with the emission peaks.
CHAPTER 5: CONCLUSION

In conclusion, a nanoheterostucture, which effectively acts as a voltage sensitive probe in aqueous media for the purpose of mapping neuronal networks within living creatures, was synthesized. This was achieved via specific stacking of semiconductor and ligand domains to spatially separate photoinduced charges while maintaining photoluminescence of the QDs. It was possible to create a structure that exhibits the Stark effect under applied voltage by specifically tuning the energetics of the system.

The proposed system is perfect for biological applications as it is not only stable in water, but also shows extremely bright photoluminescence in aqueous media. The dots will continue to be fluorescent for multiple weeks in solution after shells are grown, and were found to be non-toxic. This system is one of a very few QD approaches to biolabeling, and it has the potential to grow into an extremely useful tool of study in neuronal systems.
REFERENCES


