Experimental Interrogation Of One-Dimensional Excitons In Cadmium Selenide And Cadmium Telluride Quantum Nanostructures

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by

Virginia Lorraine Wayman

A dissertation presented to the Graduate School of Arts and Sciences of Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

August 2012

Saint Louis, Missouri
ABSTRACT OF THE DISSERTATION

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The lengths of one-dimensional quantum wires (QWs) make them excellent candidates for implementation into devices that require charge transport over micrometer-scale distances. Additionally, their tunable band-gap energies, polarized emission, and large absorption cross sections make them quite attractive for potential use in photovoltaic and optoelectronic devices. The quantum-confined radial dimension of quantum wires increases the coulombic interaction between photo-generated excitons, and therefore increase the exciton binding energy as compared to bulk and quantum well structures. In this thesis, excitons in single one-dimensional CdSe and CdTe QWs were investigated using a combination of optical microscopy techniques. My work indicates that excitons in single quantum wires are bound at room temperature, and can behave as
quantum mechanical 1-D particles. Emission is observed from bound excitons levels within the first electronic state, and a binding energy between 57-64 meV is reported. By modifying the potential energy landscape of a wire using photo-generated excitons to fill trap sites, I show that excitons can delocalize along the length of an entire QW, with distances spanning up to 10 microns. Low temperature studies indicate that the potential energy landscape is not uniform along the length of a CdTe wire, and fluctuations in the potential are likely due to a combination of variations in the crystal structure and surface irregularities. Additionally, I show that because of their polarized emission, exciton delocalization, and tunable band-gap energies, excitons in highly efficient CdSe quantum belts can also behave as 1-D quantum mechanical particles.
Acknowledgements

The people included in this section will never know how much I genuinely appreciate them, and how much their support and guidance has meant to me. These are individuals, both personal and professional, that have made my graduate career a success.

First and foremost, I would like to thank my advisor, Professor Rich Loomis. He is an incredible scientist, a caring advisor, and certainly a unique individual. I am sure I have never, and will never, meet anyone like him again in my life. Working for Rich has been an experience- there has there never been a boring moment in our lab. If it isn’t some crazy science idea he thought of the night before (which might have seemed crazy at the time, but his ideas always seemed to pan out to something worthwhile, like the work in my dissertation), then it was him barging into lab, and firing everyone in sight. In all seriousness, Rich has challenged me to work independently, and taught me how to approach problem solving on my own, and has developed my skills as a scientist. Any problem that I have with science, no matter how little hope I have for the experiment, I always believe it will work after talking with Rich. I am confident in the work I have completed during my graduate career because of the high standards of science Rich expects. He is an incredible scientist, and I am proud to be a product of his group. I would also like to thank him for his friendship. Rich has an open-door policy for his office, and I have taken advantage of that several times during my tenure here. I am fortunate to have worked for someone who not only cares about my professional work,
but also cares about me as a person. So, thank you Rich, for everything you have done for me.

Collaborating with Professor Bill Buhro was such a privilege, and I want to thank him for being my co-advisor and a member of my committee. Our group meetings with his lab were something I looked forward to every week. I always left group meetings feeling inspired and enthusiastic about science because Bill and Rich’s passion for science. Their expertise’s are very complimentary, and a perfect match to move our science forward and accomplish our research goals. Additionally, the dynamic between Bill and Rich is enviable, and has taught me how to successfully work as a group and collaborate with others. Bill is an incredible advisor, teacher and scientist, and I am incredibly honored and proud to tell people I have worked in collaboration with his research group. The quality of science that is produced from our labs is supreme because of the work mentality and standards that Bill and Rich instill in their students.

I would like to thank the other members of my Ph.D. committee. Professor Jake Schaefer has offered me invaluable science advice during my committee meetings throughout my graduate career. I am very appreciative of his willingness to listen to my presentations, ask difficult questions, and make sure my research is headed in the correct direction. I am a better scientist because of it. I would also like to thank Professors Sophia Hayes, Viktor Gruev, and Li Yang. I understand that your schedules are extremely demanding, and I genuinely appreciate you taking the time to serve on my dissertation defense committee.
I would like to acknowledge Professor Joshua Maurer and his group members, specifically Dawn Yanker and Natalie LaFranzo. They spent their valuable time developing the photolithography experiments to make my electrode coverslips. Additionally, Josh allowed me to use his lab to clean my glass coverslips, and I am thankful to him and his group for this.

To Greg Potter and the Schaefer lab, thank you for allowing me to use your helium for my trouble-shooting and low temperature experiments.

I am undoubtedly thankful for all of the funding I have received for the past six years at Wash U. The National Science Foundation (NSF), the David and Lucile Packard Foundation (Fellowship in Science and Engineering), and the Center for Materials Innovation at Washington University have all funded my research. Additionally, thank you to the Graduate School of Arts and Sciences for the Dean’s fellowship I received in the Fall of 2011.

I would like to thank all of my group members, both past and present. To Dr. Fudong Wang, Dr. Rui Tang, Dr. Yi-Hsin Liu, Waynie Olparath, PJ Morrison, Linjia Mu, Yuanyuan Wang, and Yang Zhou, Dr. John Glennon, Dr. Todd Jaeger, Jie Wei, Kenny Buyle, Camille Makarem, Rob Burnett, Ben Hoener, and Jessica Hoy - thank you. I appreciate all of the insightful feedback at group meetings, and all of the help you have given me along the way. I would especially like to thank PJ and Fudong- you two have been instrumental in my success here. I genuinely appreciate all the hard work you dedicated towards making quality quantum-wire samples. Thank you both very much. Rob and Ben- I have thoroughly enjoyed working with you guys, and I am excited for
your futures. You two added an incredible amount of energy to the lab, and I know you will both be successful with whatever you do. I am thankful that I got to know you, and I value our friendship.

To Jessica Hoy- I am not sure I would be here without you. Our graduate careers have been complex conjugates since day one. We have struggled together with classes, research, life problems… You name it, we have discussed it. You have been my best friend through graduate school, always willing to listen to my problems, talk with me about science, and discuss crazy theories I had. I hope you know how important our friendship is to me, and how grateful I am that our paths crossed. Thank you for everything!

To all of my friends in graduate school- you know who you are. Thanks for all of the great memories, we have certainly had some fun during graduate school! I would also like to thank my softball family- especially Kristen Williams and Jen Bartels. Without softball, I’m not sure I would have been able to maintain my sanity. You guys have been great friends, and I am so lucky to have you as part of my life.

I would also like to thank my non-graduate school friends, especially Elizabeth Davenport, Kelli Bachmann, Ashley McNamara, Alexis Lorinskas, and Jessica Heiple. A lot of people say you lose touch with your friends after high school, but we continue to defy the odds. You girls mean the world to me, and I love you with all my heart! Thank you for being such an important part of my life.

To my family- my twin sister Katie, my sister Becky, brother-in-law Rob, hopeful-brother-in-law Matt, nephew Caden, and my Grandma. I love you very much,
and thank you for all of your support. To my Aunt Button- thank you for letting me live with you, and for being there, especially during my last year of graduate school, when I really needed support! To my Uncle Chip- without you, I would not have applied to Wash U. You have always been someone I admire, and someone I want to model myself after. I love you and thank you for all of your support and guidance throughout my life.

I want to especially thank my parents, Norm and Joy Wayman. You have supported me with every endeavor my entire life, always pushing me to be the best that I can be, to work hard, and to be a quality person. I am the person I am today because of you, and I would not be where I am today without you. You have always been there for me, and have always helped me to the best of your ability. I love you both very much. Thank you for everything that you are, and all that you have given me.

Finally, I would like to thank my fiancé, Stuart Rutledge. You mean the world to me, and I still can’t believe we found each other. I’m not quite sure how you have put up with me throughout these past two years of graduate school, but for some reason you decided to stick around, and I am so glad that you did! You have been such an incredible influence on my life, and I love you very much. I can’t wait to experience life with you outside of graduate school! Thank you for always being there for me, and for being who you are.
To Mom, Dad, and Stu
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Chapter 1

Introduction to Semiconductors, Quantum Confinement, Excitons, and One-dimensional Quantum Wires

Semiconductor quantum wires have an increased binding energy,\(^1\) an elongated dimension, an increased absorption cross section,\(^2\) and polarized emission parallel to the length of the wire,\(^3\) in comparison to more commonly studied semiconductor quantum dots. These attributes make them attractive candidates for numerous photovoltaic and opto-electronic devices.\(^4\)\(^-\)\(^11\) Additionally, CdSe and CdTe quantum wires can easily be synthesized with a variety of diameters that approach their respective bohr radius, exhibiting quantum confinement effects, and permitting their band-gap energies to be tunable in the visible spectrum. The subject of bound excitons in quantum wires continues to be an exciting and debated topic.\(^1\),\(^12\)\(^-\)\(^15\) This work focuses on characterizing excitons in single one-dimensional semiconductor CdSe and CdTe quantum wires.

1.1 Introduction to Semiconductors

Semiconductors are essential to the design of modern electronics and technology because their unique crystal structure allows them to possess both conductive and insulating properties. The conductivity of a material describes the movement of charged
particles in response to an applied field. The conductivity of semiconductors can easily be modified by changing different conditions, such as temperature and their purity.

Because of the ability to control the flow of electrons, semiconductors are employed in numerous technological devices, including transistors, laser diodes, computer processing circuits, telephones, computers, solar cells, radios, and integrated circuits.

Semiconductors require more energy than conductors, and less energy than insulators, to excite an electron from the valence band into the conduction band. The magnitude of the separation in energy between the highest level in the valence band and the lowest energy level in the conduction band is called the band-gap energy, $E_g$, and is dependent upon the semiconducting material.

Band gaps in semiconductors are categorized as either direct band gaps or indirect band gaps. In direct band-gap materials, the maximum of the valence band and the minimum of the conduction band occur at the same point in k-space (crystal momentum). Examples of direct band-gap materials include indium phosphide, indium arsenide, indium antimonide, zinc sulfide, cadmium sulfide, zinc selenide, cadmium selenide, zinc telluride, and cadmium telluride.

In contrast, the maximum of the valence band and minimum of the conduction band occur at different points in k-space in an indirect band gap. Thus, upon absorption of a photon, an electron would have to change momentum during a transition. This indirect transition is forbidden because the linear momentum of an electron or hole cannot change during the transition, as this would violate the conservation of energy. Since photons cannot carry crystal momentum, assistance from a phonon that is equal to the difference between the electron and hole momentum is necessary in order for an
optical transition to occur. Radiative recombination in indirect semiconductors is therefore slower versus direct semiconductors, and not usually as efficient as direct band-gap semiconductors. Common indirect band-gap materials include silicon, germanium, gallium phosphide, and aluminum arsenide. Materials made of direct band gaps, on the other hand, are essential in the growth of optoelectronics because they have a much higher probability for radiative recombination than indirect band-gap materials. Light-emitting devices and laser diodes are therefore almost always made of direct band-gap materials.

The conductance and electronic properties of semiconductors can be modified by adding a small amount of dopant to the material. For example, adding an electron-donating material, such as phosphorus, to silicon, results in a higher conductance. The electrons from the valence shell in phosphorus have energies just slightly lower in energy than the conduction band in silicon, and with a small amount of external energy (either from a photon or an applied voltage), they can travel into the conduction band of silicon, resulting in a higher conductance. This type of doped material is referred to as an $n$-type semiconductor. Adding an electron-withdrawing material to the host, such as aluminum, results in a $p$-type semiconductor. Electrons from the valence band of silicon can travel to the valence band of aluminum with a small amount of external energy, which leaves behind additional holes in the valence shell of silicon, thus increasing the electrical conductance. Joining layers of $p$-type and $n$-type semiconductors creates a $p$-$n$ junction. This technology is the foundation behind controlling conductance through electronic devices, such as diodes, photovoltaic cells, and light-emitting diodes (LEDs).
Photovoltaic solar cells absorb sunlight to convert photonic energy into electricity. The solar spectrum of the sun spans from 1 nm down to approximately 1 mm, and thus solar cell designs with high efficiency are made of a wide range of materials with different band-gap energies to maximize the absorption efficiency of the device. One of the most common ways to construct a solar cell is to use a p-type semiconductor and an n-type semiconductor. When photons are absorbed by the semiconducting material in the solar cells, electrons in the valence band are excited, and can create a current. The electrons from the n-type semiconductor can flow into electron vacancies in the p-type. Eventually, the Fermi levels of the two materials equalize, and the charge carriers at the interface, the p-n junction, can be collected. The direction of the electron current is controlled by applying an electric field to the cell. These types of solar cells have a theoretical conversion efficiency, known as the Shockley-Queisser limit.\textsuperscript{20} This theoretical value is calculated by considering the amount of electrical energy that is extracted per photon of incoming sunlight, assumes a 1.1 eV band-gap energy (the band gap energy of silicon), and takes blackbody radiation, recombination, and spectral losses into account. The limit is approximately 33.6\%, meaning 337 W/cm\textsuperscript{2} can be turned into electricity. However, only solar cells with single p-n junctions are restricted to this limit, other solar cells with multiple layers have been shown to exceed the Shockley-Queisser limit.\textsuperscript{21} The work in this thesis aims to increase the efficiencies of solar cells by optimizing absorption and charge transfer efficiencies in materials suitable for implementation into these devices.
1.2 Excitons and Quantum Confinement

Electrons can be excited within a semiconductor into the conduction band with the absorption of a photon with an energy greater than or equal to the energy of the band gap. This absorption event generates an electron-deficient region in the valence band, referred to as a hole, which behaves as a positively charged particle in an applied electric or magnetic field. When electrons and holes move throughout the crystal structure, the force between other atoms can affect their movement as they interact with (exchange momentum with) the crystal lattice. Their effective mass in the lattice is dictated by the interactions with the nuclei and electron densities, and is a fitted parameter. It is therefore different than their mass in vacuum, and is defined in units of $m_e$, where $m_e = 9.11 \times 10^{-31}$ kg. Additionally, the effective mass for electrons and holes is dependent upon the material, temperature, and crystal structure (zinc blende, wurtzite, etc.).

Effective masses were traditionally measured using cyclotron resonance, but more recently angle-resolved photoemission studies have been used to determine effective masses. The attraction between an electron in the conduction band and the hole in the valence band is an electrostatic coulomb force. If the electron and hole are bound, the neutral species is called an exciton. An exciton possesses hydrogen-like energy levels, where $E_n = E_g - E_b$, where $E_b = \mu e^4/8\hbar^2n^2$, and $E_n$ is the energy of the $n^{th}$ excited excitonic state, $E_g$ is the band-gap energy, $\mu$ is the reduced mass of the electron and the hole, $e$ is the charge of an electron, $\hbar$ is Planck’s constant, $n$ is the exciton-level quantum number associated with each electronic state, $\varepsilon_0$ is the vacuum permittivity, and $\varepsilon_{SEMI}$ is the dielectric constant of the semiconductor. At room temperature, excitons are
generally weakly bound in bulk semiconductors. For example, $E_b$ for bulk CdS is 27 meV, 5 meV for CdSe, 5.1 meV for InP, and 4.9 meV for GaAs.\textsuperscript{26} Therefore, in order to observe excitonic features in optical spectroscopy experiments, they must be performed at lower temperatures ($\approx 10$ K), where the thermal energy, $k_B T$ is much smaller in order to reduce the thermal population down to the lowest excitonic levels and to reduce broadening from phonon-related broadening mechanisms.\textsuperscript{27} The Coulombic interactions result in an equilibrium distance between the electron and hole in the ground state of a bulk semiconductor, and is called the Bohr radius ($r_B$). The value of this preferred electron-hole distance depends on the medium, and typical Bohr radii range from 2.2 nm (ZnS) to 7.5 nm (CdTe) in II-VI semiconductors, and in II-VI semiconductors they range from 11 nm (InP) to 60nm (InSb).\textsuperscript{24}

When one or more of the dimensions of a semiconductor begin to approach the Bohr radius, the electron and hole begin to behave as wave particles, trapped in a box. The electronic structure of the crystal becomes perturbed, and the electronic energy levels of the electron and holes become discrete.\textsuperscript{26,28} This behavior is known as quantum confinement effects. The energy levels of the electron and hole are analogous to the energies of the particle-in-a-box (PIAB) model.\textsuperscript{26,29} The PIAB energy model can be expressed as $E_n = \frac{n^2 \hbar^2}{8mL^2}$,\textsuperscript{30} where $n$ is the number of the quantized state, $\hbar$ is Plank’s constant, $m$ is the mass of the particle, and $L$ is the length of the box. The energy level of the excited state of an electron or hole is therefore inversely proportional to the size of the semiconductor. Thus, in a quantum confined semiconductor, the effective band gap increases, and the quantum confined semiconductor band gap is equal to $E_{g, QC} = E_{g, \text{bulk}} + \Delta E_g$, where $\Delta E_g = + \ldots$, and:
Where and are the effective masses of the electron and hole, respectively.

Therefore, since the energy of an electron or hole is inversely proportional to the size ($L$), the smaller the nanocrystal, the larger the effective bandgap.

Using the particle-in-a-box model to calculate energy levels in a semiconductor is not completely accurate. The model does not account for the coulombic attraction between the electron and the hole, and it also assumes infinite potential barriers. There have been extensive efforts focused on improving the accuracy of calculating the energies of the excited states of electrons and holes in quantum confined species, with the most accepted model incorporating the use of spherical Bessel functions.\(^\text{28, 31, 32}\)

**Figure 1.1** Illustration of the different shapes of quantum confinement.

Quantum confinement can occur in as few as one dimension in a semiconductor, or in all three dimensions, as shown above in Figure 1.1. When all three dimensions are quantum confined, there are zero degrees of translational freedom (for the electronic
wavefunction to delocalize), and the nanostructure is called a 0-D quantum dot (QD) (red sphere, Figure 1.1). With two dimensions of confinement, there is one degree of translational freedom, and the structure is called a 1-D quantum wire (QW) (blue cylinder, Figure 1.1). One dimension of confinement is called a 2-D quantum well (purple rectangle, Figure 1.1). In 1-D QWs, if the elongated dimension is short, but is still longer than \(2r_B\), the structure is called a quantum rod (QR) (short green cylinder, Figure 1.1). Depending on their length, QRs can exhibit weak confinement in the elongated dimension, as evidenced by optical extinction and emission spectra. Banin and co-workers reported the band-gap energies of InAs QRs decreased with increasing QR length/diameter ratios.\(^{33}\) As the length of the rod increased, the band-gap energy decreased and approached that of a QW. The length at which CdSe QRs achieve 2-D confinement of a true QW has been experimentally estimated to be approximately 30 nm.\(^{34,35}\) Since the bohr radius of CdSe is 5.4 nm,\(^{24}\) this length (30 nm) is surprisingly long.

Quantum-confinement effects can be observed experimentally through optical absorption and emission spectra. Buhro and coworkers performed a size-dependent analysis of CdSe QWs using ensemble absorption and emission measurements.\(^{35}\) As the diameter of the CdSe QW decreased, the energy of the optical absorption and emission features increased. In addition to increasing the effective band gap, quantum confinement effects also modifies other inherent properties of the semiconductor, including the oscillator strength of optical transitions,\(^ {24}\) the exciton binding energy,\(^ {13,24}\) and the exciton-exciton interaction which can influence the optical gain.\(^ {29,36,37}\) This in
turn makes it difficult to effectively characterize all of the different contributions to the band-gap energy shifts that result from the change in dimensionality.

The exciton binding energy in quantum-confined semiconductors is enhanced with respect to bulk.\textsuperscript{1, 26, 38-41} As the dimensions of the semiconductor approach that of the Bohr radius, there is an increase in the overlap of the electron and hole wavefunctions. Since the coulombic attraction ($F = k_e q_1 q_2 / r^2$) is inversely proportional to the mean distance between the electron and the hole wavefunctions, $r$, decreasing the distance between the electron and hole wavefunctions increases the coulombic attraction.\textsuperscript{38} Additionally, there is a reduced dielectric response at the surface of quantum-confined semiconductor crystals, which decreases the dielectric screening as compared to bulk.\textsuperscript{42} The smaller effective screening increases the charge interaction between carriers, which is directly proportional to the coulomb potential. However, the increase in binding energy from the smaller dielectric constant of the surrounding media is almost exactly compensated by self-interactions of electron and holes with self-image potential.\textsuperscript{43-46} Even so, increasing the confinement still increases the binding energy. Therefore, the electron and hole interaction is stronger in QWs than in quantum wells, and in bulk. (Since quantum dots have three dimensions of confinement, and the wavefunction of the electron and hole are forced to overlap in all dimensions, there is a current discussion as to whether or not the electron and hole should be referred to as a “bound” exciton.)

Excitons in semiconductors can recombine radiatively, emitting a photon near the band-gap energy. This process, known as photoluminescence (PL), is fairly efficient in semiconductor quantum dots.\textsuperscript{47-50} The PL efficiency of a material is called the
photoluminescence quantum yield ($\Phi_{\text{PL}}$), which is the number of photons emitted per the number of photons absorbed. In CdSe QDs, $\Phi_{\text{PL}}$ can routinely reach over 60%.\textsuperscript{51-53} For semiconductor QRs, the values of $\Phi_{\text{PL}}$ are lower than that of QDs (20 – 30 %).\textsuperscript{54, 55} Reported values of $\Phi_{\text{PL}}$ for semiconductor QWs are even lower (0.1 – 0.5 %), presumably due to the increased surface area of these nanostructures.\textsuperscript{12, 14, 56-59}

The $\Phi_{\text{PL}}$, emission energy, and lifetime of core semiconductor nanocrystals can be modified by growing an epitaxial-type shell of another type of semiconductor material, creating a core/shell nanocrystal. The shell provides a barrier between the core and the surrounding medium, and can passivate surface trap states, thus increasing the $\Phi_{\text{PL}}$, and make the nanocrystal less sensitive to surface chemistry, photo-oxidation, and environmental changes.\textsuperscript{60} The growth of an epitaxial shell of a different material onto the surface of a nanocrystal can result in a modification to the band-gap energy of the nanocrystal. Generally, one of four scenarios is possible, as shown in Figure 1.2. In type I nanocrystals, the band gap of the shell material (gray rectangles in Figure 1.2) is larger in energy than the band gap of the core (blue square in Figure 1.2). Thus, both electrons and holes are confined in the core. With type II nanocrystals, either the valence band of the shell energetically overlaps with the band gap of the core material (middle illustration, Figure 1.2), or the conduction band of the shell energetically overlaps with the band gap of the core (right illustration, Figure 1.2). If the valence band of the shell energetically overlaps with the band gap of the core, electrons are not localized to the core, and can delocalize into the shell of the nanocrystal. If the conduction band of the shell energetically overlaps with the band gap of the core, then holes can delocalize into the shell of the nanocrystal.
Figure 1.2 Schematic of Type I and II band-gap energies in core/shell semiconductor nanocrystals. The upper and lower edges of the rectangles correspond to the positions of the conduction band and valence bands respectively. The inner blue squares represent the position of the band gap of the core, and the outer gray rectangles represent the shell.

1.3 One-Dimensional Quantum Wires

One-dimensional (1-D) QWs are analogous to the structure of a cylinder, where there is confinement in two dimensions (the x- and y- radial dimensions), but bound excitons are free to move along the length dimension of the nanostructure (the z-axis). As the length of the 1-D nanostructure increases, the surface area that may be sampled by an exciton increases. The properties of a nanostructure, including surface passivation and defect sites, are believed to dictate the $\Phi_{PL}$ of these nanostructures, as well as the conductivity within them. Additionally, in comparison to QDs, where the electron and hole wavefunctions are forced to overlap, the probability of radiative recombination in QWs, where the electron and hole wavefunctions are separated by the Bohr radius, is
predicted to be lower.\textsuperscript{12, 14, 56-59} Values of the $\Phi_{\text{PL}}$ for QWs reported in the literature are less than 0.5\% while those of 0-D QDs, as stated above, are much higher, and routinely reach over 60\%.\textsuperscript{51-53}

CdSe quantum belts (QBs) are a 1-D nanostructure with a shape that is very similar to a QW (they will be discussed in detail in Chapter 7). They have a reported $\Phi_{\text{PL}}$ as high as 30\%.\textsuperscript{61} These structures are technically defined as 1-D because they are confined in 2 dimensions, the thickness and width, and have an elongated dimension, with lengths ranging from 0.5 – 1 µm. This shorter length (in comparison to QWs) reduces the surface area, which decreases the sampling of trap sites by excitons. Thus, their PL QYs are higher than that of QWs since there are fewer possibilities for non-radiative recombination. However, they differ from QWs because they are not a pure cylinder shape, rather their 2-D confinement is due to a strong-confined thickness dimension (1 – 2 nm), and a weakly-confined width dimension (7 – 15 nm). Even so, optical studies have confirmed that these structures behave as 1-D structures.

Although the increased surface area in QWs gives rise to lower PL QYs, the absorption cross section increases as a result of the significantly larger volumes for these nanostructures in addition to a slight enhancement in the transition strength due to the permanent dipole moment associated with 1-D QWs.\textsuperscript{2} Experimentally measured absorption cross sections for CdSe and CdTe QWs are 4 – 5 orders of magnitude larger than those for corresponding colloidal CdSe and CdTe QDs.\textsuperscript{2} Even when volume differences are accounted for, QW cross sections are larger by up to a factor of 8.\textsuperscript{2} This enhancement of absorption, in addition to their size-tunable energy spectra, makes them especially attractive for integration into photovoltaic solar cells.\textsuperscript{8, 62}
The exciton binding energy \((E_b)\) and oscillator strengths in 1-D structures are increased as compared to less confined structures.\(^{38}\) In an ideal QW, \(E_b\) is defined as \(E_b \propto \text{Ry}^* \left[ \ln(R/\ell) \right]^2\), where \(R\) is a wire radius and \(\text{Ry}^*\) are the effective atomic units in a bulk.\(^1, 63\) Binding energies for 1-D systems are predicted to be tens of meV’s for typical QWs.\(^1, 40\) However, in the instance where the semiconductor material is embedded in an insulator with a smaller dielectric constant, the values for \(E_b\) can be significantly increased.\(^63, 64\) In GaAs, CdSe, and InP QWs with a diameter of 4 - 6 nm, binding energies were calculated to range from 120 meV- 260 meV.\(^40\) In this study, the QWs were crystallized in a transparent dielectric matrix, chrysotile asbestos nanotubes.\(^40\)

The wave function of a bound exciton in a 1-D QW can be written as a product of the wave functions representing the electron, the hole, and the wave function defining the exciton motion along the length of the QW.\(^65-67\) Thus, the wavefunction can be written as follows: \(\Psi(x_e, y_e, x_h, y_h, z, Z) = \psi_e(x_e, y_e) \psi_h(x_h, y_h) \phi(z) e^{\pm iKZ}\), where \(Z\) represents the position of the center of mass of the exciton, \(z = z_e - z_h\) represents the positions of the electron and hole along the length of the QW, \(\phi(z)\) represents the wave function of the electron-hole interaction along the length of the QW, and \(e^{\pm iKZ}\) represents the propagation of the exciton along the length of the QW.\(^65\) In an ideal 1-D system where a QW has a smooth exciton potential without any irregularities, this wave function is not perturbed, and excitons can behave as a free particle along the length of the QW. As a result, there is an equal probability of finding a 1-D exciton anywhere along a QW.

Traditionally, QDs have been used to engineer assemblies that require efficient charge transfer over nanoscale lengths.\(^68\) This is because of their ease of synthesis and size-controlled spectral tunability. However, energy loss from charge hopping events
remains a prominent problem with the use of QDs. Semiconductor QWs provide a promising alternative as a structure that can efficiently transport charge.\textsuperscript{69} Like QDs, the energy spectra of QWs can be tuned by varying the QW diameter. Additionally, the elongated dimension of QWs can reach lengths > 10 μm, which allows for efficient transport of charges across large distances.

Since the Bohr radius of CdSe QWs is 5.4 nm, QWs with diameters of approximately 11 nm or less are necessary for quantum confinement.\textsuperscript{35} Using the solution-liquid-solid (SLS) synthetic technique, QWs with diameters of 5 – 20 nm can routinely be synthesized.\textsuperscript{70-72} Extracting information from optical measurements of explicit details of the charge-carrier interactions in QWs is not always straightforward because of the existence of sample polydispersities. This is especially true for measurements of ensembles of QWs suspended in solution since standard deviations in CdSe QW diameter distributions can range from 10 to 20% of mean diameters.\textsuperscript{35} Some aspects of heterogeneous broadening can be overcome by spectroscopically interrogating single wires. Additionally, single-wire studies are used to observe important spectral properties such as PL intermittency, spectral wandering, intrawire PL intensity fluctuations, and polarization. The PL emission from CdSe QWs is in the visible region of the solar spectrum, and is generally between 650 and 700 nm, depending on the diameter of the QW. With this band-gap energy, CdSe QWs are easy to excite using common diode lasers, and optical microscopy studies of QWs are easily performed since the emission is in the visible region.

In this thesis work, I will interrogate the interactions of photogenerated electrons and holes in 1-D semiconductor nanostructures. Specifically, I will show that
photogenerated electrons and holes are indeed bound even at room temperature. I will also show that emission from different exciton levels can be observed, and the energetics of these levels can be used to estimate a binding energy of approximately 55 meV. In addition, I will show that bound 1-D excitons can delocalize along the entire length of 1-D quantum nanostructures, with distances spanning 10 μm.
1.4 References


2.1 Synthesis of CdSe QWs

The growth of nanowires has traditionally employed the vapor-liquid-solid (VLS) mechanism, developed by R. S. Wagner and W. C. Ellis in 1964. The VLS mechanism uses a vapor-phase precursor, a liquid catalyst droplet, and results in a solid crystalline product. In the work performed by Wagner & Ellis, the VLS mechanism is demonstrated by the growth of silicon whiskers. First, a small droplet of gold is deposited onto a silicon substrate. The Si substrate is heated to 950 °C, forming a small liquid alloy droplet of Au-Si. Then, a vapor mixture of hydrogen and SiCl$_4$ is introduced to the alloy droplet/substrate. This adsorbs onto the liquid Au-Si alloy surface, and Si supersaturates the droplet. The Si supersaturated alloy droplet nucleates into a Si whisker as axial crystal growth occurs, and Si nanowhiskers grow until the Au is consumed, or the growth conditions are changed. Unfortunately, the VLS growth mechanism results in mean diameters that are greater than 100 nm, and there is a wide diameter distribution.

The first report of the growth of semiconductor nanowires using the VLS method was in the early 90’s, and diameters of less than 20 nm were achieved. However, because the authors used metallic catalyst droplets without any real way to control their size, the diameter distributions were broad. Other important studies towards the optimization of semiconductor nanowire growth through the VLS mechanism were made
Notably, Yang and coworkers used the VLS growth mechanism to synthesize ZnO nanowires with good crystalline quality and good diameter control.\textsuperscript{13}

A modification to the VLS synthetic technique resulted in a new and exciting synthetic mechanism for semiconductor nanowires. The solution-liquid-solid (SLS) mechanism is analogous to the VLS technique, except that it employs the use of a catalyst particles with melting points below 400 °C.\textsuperscript{3,14} This growth mechanism has shown to produce nanowires that are soluble, have smaller diameters, and have smaller diameter size distributions. Additionally, the synthesis itself is easier to perform than the VLS method because introducing a vapor-phase compound to a synthesis often requires specialized laboratory apparatuses. On the other hand, VLS growth affords the higher crystalline nanowires, but they are also grown without surfactants, which affects their photoluminescence properties and solubilities. Thus, their potential for implementation in various opto-electronics and photovoltaics that require efficient charge transport and luminescence is likely not as high as nanowires synthesized using the SLS method.

The synthesis of CdSe QWs using the SLS mechanism has been described in detail in numerous publications.\textsuperscript{3,14-18} In SLS synthetic growth, nanowire diameters are controlled by the diameter of the seeded catalyst, and the reaction temperature.\textsuperscript{3} Monodisperse Bi nanoparticles are used as the seed to catalyze CdSe wire growth.\textsuperscript{18,19} Nanowire diameters increase linearly with the diameter of the catalyst nanoparticle.\textsuperscript{3} To synthesize CdSe quantum wires, CdO (cadmium oxide, 10 mg, 0.078 mmol), OA (oleic acid, 53 mg, 0.19 mmol), TDPA (tetradecylphosphonic acid, 10 mg, 0.036 mmol), DOPA (di-n-octylphosphinic acid, 10 mg, 0.034 mmol), and purified or 99% TOPO (tri-n-
octylphosphine oxide, 5 g, 0.21 mmol) are loaded into a 50-mL Schlenk reaction tube. Monodisperse Bi nanoparticles (23 mg, 0.00092 mmol of Bi atoms), TOPSe (trioctylphosphine selenide, 500 mg, 1.1 mmol) and TOP (trioctylphosphine, 100 mg, 0.27 mmol) are combined together in a separate vial, which is capped by a rubber septum, and are loaded into a syringe. The Schlenk tube is degassed under vacuum at 100 °C for 15 minutes, back-filled with N₂(g), and then inserted into a 320 °C salt bath until the solution is clear. Then, the Schlenk tube is switched to a cooler salt bath, 250 °C (the temperature of the salt bath is dependent on the Bi nanoparticle size). The Bi nanoparticle, TOPSe and TOP mixture is quickly injected into the Schlenk tube. The reaction mixture will turn a reddish-brown color within a matter of seconds, and the tube should be withdrawn from the bath after 5 minutes and allow to cool to room temperature. Wires are isolated as a brown precipitate by adding a 5:1 ratio of toluene to methanol, followed by centrifugation, and decanting of the supernatant. The wires are redispersed in toluene, and are a uniform and clear light-brown color. They are stored at room temperature, in TOPO.

Using the SLS synthetic mechanism, CdSe wire diameters can range from about 5 – 15 nm, with standard deviations in the diameter distributions between 11 – 17%. The lengths of the wires can be as long as 10 μm. Wire diameters are generally determined using transmission electron microscopy (TEM). CdSe wires have a wurtzite crystal structure, as determined by electron diffraction patterns. A TEM image of CdSe QWs is included in Figure 2.1.

Other research groups have been successful with synthesizing 1-D CdSe nanowires. Kuno and coworkers used bimetallic Au-Bi core-shell particles to synthesize
CdSe nanowires using the SLS mechanism.\textsuperscript{20,21} Mews and coworkers employed the SLS mechanism to grow CdSe nanowires with an admixture of wurzite and zinc blende.\textsuperscript{22,23} Penner and coworkers prepared CdSe nanowires using a lithographically patterned nanowire electrodeposition method.\textsuperscript{24,25}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{TEM_image.png}
\caption{TEM image of CdSe QWs (courtesy of PJ Morrison, Buhro group).}
\end{figure}

2.2 Ensemble Absorption and PL measurements

An absorption spectrometer with a dual-beam arrangement was used for ensemble absorption measurements. Two different light sources are employed to cover the UV and visible/NIR (near infrared) regions; a deuterium lamp is used for the UV region, while a tungsten/halogen lamp is used for the visible/NIR light source. Near-monochromatic light is selected by passing the light source through a monochromator. Photodetectors behind the sample and the reference sample detect transmitted light, and the recorded ratio $I/I_0$ is the absorbance value.
To take an absorption spectrum, three different cuvettes are required; two solvent cuvettes and one cuvette containing the sample. The two solvent cuvettes are used to normalize the intensities between the reference beam and the sample beam. Then, the sample cuvette and solvent cuvette are used for the actual absorption scan. Usually, scans are taken using 0.5nm step size with 200 msec integration time at each step, and 2 nm slit widths, though these options can be modified to fit the experimental need. Cuvettes used in these experiments are made of quartz and are matched, meaning every face of the cuvette has the exact absorption value (if the sample absorbs in the NIR region, a different material is needed). For the nanomaterials studied in this work, absorption values are kept between 0.07 – 0.12 to avoid reabsorption processes.

Ensemble PL measurements were taken using a standard emission spectrometer. Only two cuvettes are needed for this measurement, a cuvette containing the solvent, and a cuvette containing the sample. The PL from the solvent is necessary to establish a baseline, and this spectrum is then subtracted from the PL spectrum of the sample. PL spectra for both the sample and the solvent are recorded using identical settings. Typical emission settings used 5.0 nm slit widths, and a slow scan rate (1.0 nm step/500 ms). It is especially important in ensemble emission measurements that the absorption value is between 0.07 – 0.12 so that front-face effects do not occur. If the concentration is too high, the intensity of the excitation light is not constant throughout the cuvette because the absorbing molecules in the front part of the cuvette absorbed or scattered much of the excitation light. As a consequence, emission is not uniform throughout the sample, which can lead to an erroneous detection intensity. Thus, for a reliable emission reading, it is necessary to have the appropriate concentration.
2.3 Optical Microscopy

PL microscopy is an optical microscopy technique that uses emission, as opposed to transmitted light, to generate an image. In traditional microscopy measurements, a sample is deposited onto a coverslip, and illuminated with light that is an appropriate wavelength to optically excite the sample. PL is then collected through the objective, and can be imaged by using a CCD camera or some other form of optical detection. To illuminate the sample, the light source can either be placed above or below the sample. Inverted microscopes are often used to employ the technique of epi-fluorescence microscopy. In this type of microscopy, the excitation light is focused onto the sample through the same objective that is used to collect sample fluorescence. A typical epi-fluorescence microscopy setup is shown in Figure 2.2.
Figure 2.2 Experimental layout of an epi-fluorescence optical microscopy setup in an inverted microscope arrangement.

As shown in Figure 2.2, light from a laser source travels through a neutral density (ND) filter, then passes through a 2” focal length plano convex lens (CL), a pinhole (PH), and a second 8” focal length plano convex lens, before entering the microscope. The ND filter cuts down the excitation power, thus enabling precise control over the number of photons hitting the sample per unit time and area. The diameter of the pinhole used for this setup was 30 μm, and the pinhole was placed at the focal plane of the first convex lens. This pinhole is used to create a light point source, thereby eliminating out-of-focus light that does not originate from the focal point of the lens. The second convex lens is used to create parallel light into the microscopy apparatus. It is important to optimize the position of the second convex lens to ensure that the incident light on the microscope is parallel, and to achieve a diffraction-limited spot size on the sample. As a practical point,
the moving of the lens away from the focal distance will increase the illumination spot and decrease the spatial resolution of the excitation. On occasion, we purposely impose this condition in order to illuminate larger spatial regions of the sample. A significantly better detection resolution can still be obtained with proper focusing of the microscope objective lens. Excitation light enters the microscope, reflects off the dichroic mirror, and excites the sample. A long-pass (LP) filter is used to filter the light collected by the objective that passes through the dichroic mirror to selectively detect emission and not scattered light. Single-QW experiments are performed using an inverted Nikon TE2000-E microscope. The transmitted light is then transmitted through a Nikon microscope. It is possible to image the samples by using a mirror or to spectroscopically resolve a spatial region using a grating. The images or spectra are imaged with a Photometrics Coolsnap CCD camera, with a 1392 x 1040 imaging array, with a wavelength range of approximately 400 nm – 730 nm.

Samples are prepared by spin-coating a dilute solution of CdSe QWs onto a No. 1.5 glass coverslip. The microscope objectives used are either a Nikon Plan Apo VC 100x/1.4 numerical aperture (NA) oil objective, or a Nikon Plan Apo 40x/0.95 NA short working distance (140 μm) objective. Typically, a 488 nm continuous wave (cw) diode laser is used for excitation, although a 532 nm cw diode laser and a 405 nm cw diode laser are also used. There is approximately 18 mW of power from the 488 nm cw laser, 22 mW for the 532 nm laser, and 30 mW for the 405 nm laser. PL images and spectra are obtained by using a 2300i-series photospectrometer from Princeton Instruments/Acton, with an ES series Photometrics Coolsnap CCD camera. The monochromator has an interchangeable turret with a 150 g/mm grating and a 300 g/mm grating, which are used
to acquire spectra, and a mirror, which is used to acquire an image. A PL microscopy image of CdSe QWs is shown in Figure 2.3. This image was recorded using 488 nm excitation, with a 40x 0.95NA objective. LabView software is used to operate the monochromator and camera, and collect data. Common exposure times of 100 ms and 1 sec are used to collect images and spectra, respectively. However, exposure times are dependent upon the fluorescence intensity of the sample, and are frequently changed to accommodate the efficiency of different samples.

**Figure 2.3** A PL microscopy image of CdSe QWs. Image recorded using 488 nm excitation, with a 40x 0.95NA objective.
2.4 Time-Resolved Studies

PL lifetime measurements were performed by using time-correlated-single-photon-counting (TCSPC). This technique uses a sensitive detector to record low-intensity light signals with ps time resolution. A short-pulse laser (< 200 fs) excites the sample, and the detector measures the time delay of individual photons from the excitation pulse.

The pulsed-laser used for excitation is a tunable Spectra Physics titanium sapphire oscillator laser system, 710 – 990 nm. A photo-acoustic optical modulator system, is used to control the excitation rate, 81.5 MHz – 10.2 kHz, and to frequency-double the excitation source. The resultant pulse widths are less than 200 fs. The pulsed-laser beam is then aligned into the optical microscopy setup described in section 2.2, in order to excite the sample. The rate of photons emitted as a function of time from a sample can be imaged through the spectrophotometer, or they can be aligned into a microchannel-plate photomultiplier-tube (MCP-PMT) to detect photons as a function of time. The output of the MCP-PMT is fed into a Becker-Hickl SPC-830 TCSPC card.

2.5 Preparation of Electrode Coverslips using Photolithography

In order to interrogate the role of separate charge carriers on the PL detected from single CdSe QWs, PL images and spectra were recorded as a function of electric-field strength. Single QW experiments were performed using glass coverslips patterned with
indium tin oxide (ITO) electrodes using a lift-off photolithography process.\textsuperscript{26} The electrode coverslips were necessary to provide an electric field about single CdSe QWs. First, positive photoresist S1805 was spin-coated onto a glass No. 1.5 square coverslip. Then, a mask with the electrode pattern was placed over the coverslip and exposed to Hg light filter with a 365 nm bandpass filter for approximately 30 seconds. The coverslip was then placed into a solution of MF-321 (metal free), which removed the soluble polymer, leaving the outline of the electrode pattern onto the surface of the coverslip using electron beam evaporation. Then, the coverslip was rinsed in a solution of resist strip (which removed the remaining photoresist), leaving the ITO pattern on the glass. A PL microscopy image of the electrode is shown in Figure 2.4. Panel A is an image of just the electrode pattern, recorded using a 4x objective. The lighter-contrast outline of the electrode pattern is the glass, while the dark pattern is the ITO on the glass coverslip. Panel B is an image of CdSe QWs spin-coated onto the electrode-pattern. This image was recorded using a 40x, 0.95NA Nikon Plan Apo objective. Again, the lighter contrast represents the glass, while the darker contrast represents the ITO.

![PL microscopy images](image)

**Figure 2.4** PL microscopy images of A) the electrode pattern, taken using a 4x objective, and B) CdSe QWs spin-coated onto the electrode pattern, taken using a 40x objective.
Electric-field experiments used micro-positioners with tungsten needles from Quarter Research and Development (ModelXYZ300 TR and XYZ300TL) to make contact with the lead pads on the electrodes. A function generator (Standard Research systems, Model DS340) was used to apply a square or sine wave voltage. A maximum voltage of 19.0 V (±9.5 V) was applied to the electrodes, with gaps between the electrodes equal to 30 μm. The magnitude of the electric field was 3.2 kV/cm. With the electric field on, data was taken following standard optical microscopy procedures described in section 2.3.

2.6 Exciton-Delocalization Experiments

Exciton-delocalization experiments employed the use of two excitation sources to illuminate a single QW at one time. The experimental setup is shown in Figure 2.3. The first excitation source was a cw 488 nm diode laser to wffluoresce CdSe QWs, employing power densities between 50 – 500 W/cm². The second excitation source was a cw 405 nm diode laser, and was used to epi-illuminate the sample, with typical power densities of 1 – 50 W/cm². This illumination source was focused down to a diffraction-limited spot. The best spot size achieved was approximately 425 nm in diameter. As discussed in section 2.3, light is collected through a short working distance (140 μm) 40x, 0.95 NA Nikon Plan Apo objective, and aligned into a spectrophotometer to record images and spectra.
LabView software is used to control our spectrophotometer and collect data. The standard data collection program was modified to accommodate the use of two excitation sources. Electronic shutters were programmed with LabView software to allow for easy switching between excitation colors. All images were acquired using an exposure time of 100 ms. The program was designed as follows. First, a single QW was illuminated with $\text{w}f$ excitation only (488 nm) for 60 seconds, and an image was recorded. (We chose to start our data collection only after the QW was illuminated for 60 seconds because there is often a fast photo-enhancement in the photoluminescence of QWs that is typically 45 seconds. Since we are ultimately comparing PL intensities in this experiment, we wanted the PL to be as steady as possible.) After an image was taken using only 488 nm excitation, an image using both excitation sources was taken. Lastly, a third image was taken using only 405 nm excitation.
Figure 2.3 Microscopy setup for exciton delocalization experiments.

2.7 Low Temperature Studies

To further investigate the potential energy landscape of quantum wires, experiments were performed at low temperatures ($T \approx 4$ K), where the thermal energy, $k_B T$, is much lower. An Oxford instruments Microstat HighRes II continuous flow liquid helium cryostat was used to achieve cryogenic temperatures. Continuous flow cryostats use an oil-free pump to draw liquid helium from a storage dewar to cool the sample. The helium is transferred to the cryostat through a transfer tube. Once liquid helium reaches
the cold finger in the sample cell, it is returned through an outer chamber within the cryostat and the transfer tube, where it acts as an additional means to cool and insulate the cryostat and transfer tube. The temperature is controlled by a combination of a manual control valve on the transfer tube regulating the flow of helium, and an electrical heater that resides within the sample chamber, which is manually controlled using an electronic temperature control box. An oil-free turbo-molecular pump is used to evacuate the cryostat and transfer tube to vacuum, usually to pressures of $10^{-6}$ mTorr. Images and spectra were acquired using a long-working distance objective (3.6 - 2.8 mm), 40x 0.60NA Nikon Plan Fluor objective.
2.8 References


Chapter 3

Bound 1-D Excitons in Single CdSe Quantum Wires

3.1 Introduction

Semiconductor QWs are increasingly being studied due to their large absorption cross section (x8 bigger per unit volume in comparison to quantum dots (QDs),\textsuperscript{1} tunable band gap energies,\textsuperscript{2} and one-dimensional (1-D) shape that allows for charge transfer. Even with their low photoluminescence quantum yields $\Phi_{PL}$, QWs have shown promise for applications in electronic and solar technology.\textsuperscript{3,4} With lengths on the average of tens of microns,\textsuperscript{2,5} these structures are the optimal distance to allow for efficient charge transport in photovoltaic and optoelectronic devices.\textsuperscript{6}

The wavefunction used to define a 1-D QW includes components that make up the electron and hole wavefunctions in the radial dimensions, multiplied by components representing the electron and hole pair in the $z$-dimension (the long axis). For a perfect QW, the total exciton wavefunction can be written as:

$$\Psi(x_e, y_e, x_h, y_h, z) = \Psi_e(x_e, y_e) \Psi_h(x_h, y_h) \phi(z) e^{\pm ikZ}. $$\textsuperscript{7} In this equation, $\Psi_e(x_e, y_e)$ represents the wavefunction of the electron in the $x$ and $y$ dimensions, $\Psi_h(x_h, y_h)$ represents the wavefunction of the hole in the $x$ and $y$ dimensions, $\phi(z)$ represents the coulombic interaction between the electron and hole in the $z$ dimension, and $e^{\pm ikZ}$ represents the free wave behavior of the electron/hole pair along the $z$-dimension.\textsuperscript{7-9} The probability of finding an exciton along a 1-D QW is achieved by squaring the total wavefunction, and is equal to a constant. Thus, there is an equal probability of finding an exciton anywhere along an ideal 1-D QW.
The discussion of the existence of 1-D excitons has recently been gaining momentum.\textsuperscript{10-12} Results from the Buhro and Loomis laboratories suggest that following the absorption of above band-gap photons, 1-D excitons are formed in CdSe QWs, and these electron-hole pairs largely remain bound at room temperature. First, in order for high $\Phi_{\text{PL}}$'s to be achieved, values higher than 20\% have been reported,\textsuperscript{13} it is unlikely that separate charge carriers would be formed; the propensity for radiative recombination would be very low for separate charge carriers, and non-radiative Auger rates would become high. Second, the observation of synchronous PL intensity blinking spanning entire CdSe QWs,\textsuperscript{13} suggest that once non-radiative trap sites are filled the 1-D nature of the excitons is observed with nearly equal PL intensity observed along the length of the entire QW. As I will present in Chapter 4, emission can be detected from multiple exciton levels, and the energies of these levels indicate a binding energy of 57-64 meV.

The Kuno group reported that the PL intensity along a single CdSe QW with diameters between 5 and 12 nm could be steered using an external electric field.\textsuperscript{14} In that work, they observed that the PL intensity would increase at the end of a QW closest to the negative electrode. Electric fields up to 30 kV/cm were used in these experiments, which are not sufficient to dissociate electron-hole pairs if the excitons are bound at room temperature.\textsuperscript{15,16} However, they saw emission steering with an electric field strength of $<4$ kV/cm. They concluded that there are some charge carriers present within the QWs, and additional charges are photo-generated. In a subsequent report, the Kuno group reported that excitons may be bound at RT in QWs with diameters as large as 10 nm.\textsuperscript{17} This recent work was focused on measuring the extinction spectra of single CdSe QWs. The spectra included at least three electronic transitions, and in modeling the spectra an
exciton binding energy was included to achieve a sufficient simulation. Specifically, they reported that the exciton binding energies range from 100 to 300 meV with decreasing diameter. While the simulations do support the notion of enhanced electron-hole Coulombic interactions, to the point that they may be bound as 1-D excitons, similar experiments to those initially performed by the Kuno group using electric fields to test for separate charge carriers\textsuperscript{14} would confirm that 1-D excitons are photo-generated with above band-gap excitation. If bound excitons are present, the presence of an electric field should not affect neutral excitons and no PL steering should be observed, as long as the strength of the electric field is smaller than the binding energy. The PL should therefore remain unchanged.

Since the PL properties of semiconductor nanostructures are extremely sensitive to the environment, particular attention was given to the preparation of the samples in these studies. Specifically, the values of $\Phi_{\text{PL}}$'s for both QDs\textsuperscript{18,19} and QWs\textsuperscript{13} are extremely sensitive to the ligand passivation of the semiconductor nanomaterials. Additionally, the general trends for PL steering reported by Kuno changed with the solvent environment of the sample.\textsuperscript{14} While excess electrons were present in the CdSe QWs prepared in toluene, the observed dynamics suggested holes when oleyl amine or immersion oil was used as the solvent. In the work presented in this chapter, I first investigate the effects of an electric field on the PL intensity in single CdSe QWs that were carefully diluted in toluene to decrease the concentration of other compounds, which most likely are left over from the synthesis. Similar experiments were then performed with higher QW concentrations that have additional compounds from the synthesis remaining, in order to investigate their effects on PL steering.
3.2 Experimental

CdSe QWs were synthesized using the SLS-synthetic technique described in Chapter 2.1.2,5,20 Optical microscopy experiments were performed using the procedure described in Chapter 2.3. Electrode-coverslips were made using standard photolithography techniques as outlined in Chapter 2.5. The distances between the electrodes were 30 μm. PL images and spectra were acquired using 488 nm (2.54 eV) excitation, with a range of power densities of 5 to 500 W/cm². QWs chosen for analysis in this study were not blinking, however, previous work in our lab has identified that whole QW blinking favors this power range.13 Indeed, a few individual QWs did exhibit blinking, although they were not included in the analysis. Both square-wave and sinusoidal voltage signals, with values of -9.5 to 9.5 V, were applied to the electrodes in order to achieve ac electric fields of -3.2 kV/cm to 3.2 kV/cm. The experiments were performed under an ambient environment.

3.3 Results & Discussion

Figures 3.1A-C represent PL microscopy images of a single CdSe QW (diameter ≈ 10 nm) prepared using a “purified” dilute sample and with varying electric fields. The PL intensity profile along the QW does not noticeably vary with an external electric field; the image in panel A is with the electric field off, the image in panel B is with the electric field pointing up, and the image in panel C is with the electric field pointing down. The integrated PL intensities of the whole QW (Figure 3.1D, black trace), and the ends of the
QW (Figure 3.1E, blue and red traces), are plotted as a function of time. The electric-field strength (3.2 kV/cm with a 0.2-Hz square-wave) is plotted in purple (Figure 3.1F). The first seven seconds of the data was taken with the electric field off in order to record a background PL intensity level and to measure the magnitude of the intensity fluctuations. When the electric field is turned on, a noticeable change in the PL is not observed, and the PL remains fairly constant. There are minor intrawire intensity fluctuations, as expected for CdSe QWs, but a distinguishable change in PL correlating to the electric-field oscillations is not observed. As mentioned above, excitation power densities ranged from 5 to 500 W cm$^{-2}$ were used in these studies, and over this range no PL steering attributed to the electric field were observed. These and similar data recorded on numerous other QWs prepared from the “purified”, dilute solution, and from other CdSe QW batches, indicate that there are no, or at best minimal, separate charge carriers within the CdSe QWs.
Figure 3.1. PL Intensity of a single CdSe QW prepared from a dilute solution, in an applied electric field. (A-C) PL microscopy images of a single QW without the electric field (A), with the electric field pointing up (B), and with the electric field pointing down (C). (D) The integrated PL intensity of the entire QW shown in A-C; (E) integrated PL intensity of the top of the QW (blue) and the bottom of the QW (red); and (F) the electric-field oscillation applied to the QW as a function of time.

In contrast, single QWs prepared from a concentrated solution behave much differently when exposed to an electric field, with results closely resembling those from the Kuno group. Figures 3.2A-C include PL microscopy images of a single QW
without the electric field, panel A, with the electric field pointing up, panel B, and with the electric field pointing down, panel C. With the electric field on, the PL intensity increases at the end of the QW closest to the positive electrode, top in Figure 3.2B. With the electric field pointing in the opposite direction, the emission enhances at the other end of the QW, bottom of the QW in Figure 3.2C. This behavior, referred to as emission steering by Kuno, is clearly illustrated by plotting the integrated intensity of the PL collected from a single QW as a function of time. Figure 3.2 includes plots of the integrated intensity of the entire QW (black trace, Figure 3.2 D), and of the top and bottom regions of the QW, blue and red traces, respectively, Figure 3.2 E. The time dependence of the electric field is also shown in Figure 3.2 F for reference. This emission steering continued until the electric field was turned off, at which point the PL intensity redistributed itself along the entire QW, and the intensity resumed to the approximate level it was before the electric field was applied.
Interestingly, the total PL intensity along the QW increases when the electric field is turned on for the concentrated samples, but not the “purified”, diluted samples. This strongly suggests that the electric field is interacting with the environment of the QW, which then changes the PL properties along the QW. Rothenberg et al. observed reversible on-off emission behavior in single CdSe quantum rods (QRs) upon applying an
external electric field. In that study, some of the QRs switched off with an external electric field, while other QRs switched on with an electric field. This switching behavior was attributed to differences in the local field conditions of the single QR.

There are several factors that may be responsible for variations in the local field of a QW, including the choice of solvent, surface defects on the structure, surface ligands, and mobile charge carriers. In the work presented here, the main influence on the local environment is thought to be leftover reagents from the synthesis suspended in the solvent. Since different behavior is observed in single QWs from dilute solutions versus concentrated solutions, the concentration of other solute compounds within the sample are most likely influencing the local environment of the QWs.

The presence of these other compounds was verified using atomic force microscopy (AFM) to physically characterize the samples prepared for the optical microscopy experiments. The AFM images included in Figure 3.3 A and B are for CdSe QWs prepared on a coverslip with a concentrated sample and with a “purified”, dilute sample, respectively. Most of the QWs from the concentrated sample are encompassed by an unevenly distributed film and are not observed in the AFM image. Only a few QWs project from the film, but even these have a coating on them, as indicated by diameters that are significantly larger than observed in TEM images acquired for the same sample. The AFM images of the coverslips prepared with the “purified”, dilute sample of CdSe QWs do not have an amorphous layer over the QWs. Instead, only single QWs with heights and widths commensurate with those measured in TEM microscopy are observed.
Figure 3.3. AFM images of CdSe QWs prepared from solutions of concentrated QWs(A), and a diluted solution (B). (AFM images are courtesy of AIST-NT)

The CdSe QW synthesis employs the use of several reagents to passivate surface traps and improve the PL efficiency. Tetradecylphosphonic acid (TDPA), trioctylphosphine oxide (TOPO), and dioctylphosphininc acid (DOPA) are all used in SLS
CdSe QW synthesis. In a solution of CdSe QWs, the solvent consists primarily of toluene, but a combination of leftover ligands and bismuth salts remaining after the synthesis are also in solution. The presence of leftover synthetic reagents in solution is sometimes evidenced by the presence of a high-energy background signal present in ensemble CdSe QW PL spectra. This background signal is rarely present in single CdSe QW PL spectra, and when it is present, it quickly photobleaches. Rui Tang in the Buhro group has found that one of the compounds responsible for the high-energy PL background is a Bi$^{3+}$-TOP complex.

The strength of the electric field, 3.2 kV/cm, is not enough to overcome the binding energy and dissociate the exciton. In a study conducted by Miller and co-workers, a shift in the exciton peak to lower energy is expected as the electric field begins to approach the strength of the binding energy.$^{15}$ In quantum-well structures, only at field strengths of approximately $10^2$ kV/cm did they observe evidence indicating the electric field influenced the exciton binding energy. Therefore, if an exciton is influenced by the electric field, a shift of the exciton peak to lower energies should be observed. Figure 3.4 is spectra of a single CdSe QW recorded with the electric field on (red), and with the electric field off (black). It is clear from this graph that the PL feature does not shift in energy with the field on; only subtle changes are observed in the PL spectra. The PL intensity is slightly higher with the electric field on, panel A. By normalizing the PL spectra, panel B, a small change in the lineshape of the PL spectra with the electric field on is observed, as the PL spectrum broadens slightly. This change is very subtle, however, and has been reported previously in CdSe QWs.$^{14}$ Since there is not a shift in
energy in the exciton feature, we conclude that the electric field is not strong enough to separate the bound electron/hole pair.

**Figure 3.4** PL spectra of a single CdSe QW taken with the electric field on (red trace), and with the electric field off (black trace). A) PL spectra with field on versus off, illustrating a minor enhancement of the PL intensity; B) Normalized PL spectra, illustrating a negligible change in the PL shape.

From these studies, we can draw several conclusions. First, the QWs are not permanently charged, they are neutral. If individual electrons and holes were present in QWs, then a change in emissive behavior would be observed for the QWs placed in an electric field (Figure 3.1), even for the “purified”, dilute samples of QWs, which is not observed. Since emission steering is only observed in concentrated solutions (Figure
3.2), when presumably the QWs are encompassed by a film, an external source must supply the charge responsible for the observed steering behavior. Additionally, if charge carriers were intrinsic to the QWs and not supplied by an external source, a decrease in $\Phi_{PL}$ would be expected on the other end of the wire towards the negative electrode (away from the enhancement). This is because a charge rearrangement towards the positive electrode would leave behind open trap sites, and increase the probability for non-radiative recombination, thus decreasing the QY on the other end of the QW away from the enhancement. This is not observed. Instead, the QY for the entire QW increases in an electric field, as shown in Figure 3.2 D. Also, the makeup of the film is thought to be leftover synthetic reagents, most of which are of acidic nature, which explains why the QWs behave as though there is an excess of electrons present (the PL localizes towards the positive electrode).

The second, very important conclusion we can make from these data is the existence of bound 1-D excitons, even at room temperature. Since emission steering is not observed in dilute QWs, photogenerated excitons must be bound. Even with lower field strengths employed in this study (3.2 kV/cm), if individual charge carriers were present, they would localize towards their respective electrode, as evidenced in Figure 3.2.

Emission steering in CdSe NWs has been previously observed. The authors in that study hypothesize that the passivation of electron acceptor states by individual charge carriers causes the PL QY of the NW to increase at the end closest to the positive electrode. The authors also observed a change in emission behavior with different solvents. When NWs were dispersed in oleic acid and immersion oil, the PL localized
towards the negative electrode, suggesting an excess of holes were present in the NW. This information supports our findings that QWs are not permanently charged, and that bound 1-D excitons are present at room temperature in CdSe QWs. It does not support their main conclusion that there are separate charge carriers in CdSe QWs, and that additional charge carriers are photogenerated when exciting with above band-gap photon energies. If individual charge carries were intrinsic to the QW, then emission steering would be observed in all single QWs, both in dilute and concentrated solutions, and should not be as sensitive to the solvent.

3.4 Conclusion

In conclusion, the emission behavior in single CdSe QWs is dictated by the local environment. In concentrated solutions, leftover synthetic reagents in solution form a film that encompasses QWs, supplies excess charge, and is responsible for emission steering observed when the QWs are exposed to an external electric field. Diluting the solution reduces the density of the leftover synthetic reagents, and the film is not present. This changes the local environment, and emission steering is not observed. Based on our results, we conclude that QWs are not permanently charged, and photogenerated excitons are bound.
3.5 References


Chapter 4

Bound Exciton Levels in One-dimensional Single Semiconductor Quantum Wires

4.1 Introduction

The ability to tune the band-gap energies of semiconductor quantum dots (QDs) and quantum rods (QRs) by varying the diameters of the nanostructures is being utilized in photovoltaic (PV) devices in order to enhance efficiencies across broad regions of the solar spectrum.\textsuperscript{1-3} In attempts to increase the efficiency of these devices, Type-III photovoltaics are being designed that incorporate QDs with low-energy band gaps. Along with the important gains attributed to the absorption of infrared solar emission, an additional increase in efficiency is expected if multiple excitons can be photogenerated in the low-energy nanostructures. In PbSe QDs, multi-exciton generation has been reported, where one photon produces as many as three excitons.\textsuperscript{4} While the ability to generate numerous excitons within single quantum structures offers promise for photovoltaic devices, as well as for laser-gain media, Auger relaxation is efficient in QDs and QRs and the lifetimes of the excitons decrease significantly with exciton density.\textsuperscript{5-7} As a result, it will be necessary to promptly separate and collect the electrons and hole charge carriers in order for these PV designs to be efficient. In most of the design schemes being utilized, the QDs or QRs are embedded in a conductive polymer to efficiently transport the holes to the cathode of the PV device. The electrons, however, must hop or tunnel
between the QDs or QRs prior to being collected at the anode. This hopping process is not inefficient, and is an additional limitation in the efficiencies of these PV devices.²

Colloidal semiconductor QWs can be synthesized that still offer tunable band-gap energies, but have lengths that are on the order of the dimensions of the absorbing media in PV devices. The dimensionality of the QWs should also result in a decrease in the efficiency for Auger relaxation. As a result, the incorporation of semiconductor QWs in PV devices offers a route to circumvent the limitations associated with QDs and QRs. In Cartesian coordinates the quantum-mechanical wave function for an exciton in a QW can be written as

$$\Psi_{e, y, x, h, y, h, z, Z} = \psi_e \psi_h \phi \zeta^e_{Z} \zeta^h_{K}$$

with Z and z = z_e - z_h representing the center-of-mass position of the exciton along the length of the QW and the distance between the positions of the electron and hole, respectively.⁹ Since the Coulomb energy is much weaker than the single-particle confinement energy in the radial dimension of the QW, the single-particle states for the electron and hole, \(\psi_e \phi_{e} \) and \(\psi_h \phi_{h} \), can be approximated using a circular quantum well with a barrier height determined by the electron affinity. Consequently, there is quantum confinement in the radial coordinate of the QWs that provides the tunability of the energies of the excitonic states by varying the QW diameter.⁹,¹⁰

The wave function of the electron-hole interaction along the length of the QW, \(\phi \zeta_{Z} \), is dictated by Coulomb interactions. The binding energy, \(E_b \), of the electron and hole is very weak in bulk materials at room temperature. For example, \(E_b \) for bulk CdSe is 5 meV.¹¹ Enhancements in \(E_b \) can arise from the dielectric constant of the surrounding medium.¹²-¹⁵ The binding energy for materials with an insulator shells are very large, up to 260 meV.¹⁴ The bound electron-hole pair has a wave number \(K \) determined by the translational kinetic energy of the 1-D exciton, and it behaves as a ballistic, free particle,
$e^{ikz}$, with no restrictions along the length of the QW. Consequently, there is an equal probability of finding an exciton anywhere along an ideal semiconductor QW that has no significant changes or irregularities in the exciton potential energy landscape. As a result, QWs should offer a means for efficient transport of excitons or separate charge carriers spanning micrometer distances. The photophysical processes that occur within semiconductor QWs that may ruin this delocalized 1-D exciton behavior remain largely uncharacterized. For instance, little is known about the dynamics or energetics of the excited exciton levels or the varying exciton-exciton interactions that occur at high exciton densities in QWs. The spectroscopic results presented here on CdSe QWs reveal some of the properties of 1-D excitons in nearly ideal QWs.

4.2 Experimental

Colloidal samples of CdSe QWs with diameters of $\approx 10$ nm and lengths ranging from 2 to 10 $\mu$m were prepared using the solution-liquid-solid method, as described in Chapter 2.1.\textsuperscript{10, 16, 17} The PL spectroscopy of single QWs was investigated using optical microscopy techniques described in Chapter 2.3. PL spectra were studied as a function of power density using cw excitation at 2.33 eV (532 nm). Since the excitation photons are considerably higher in energy than the band gap, $\approx 1.8$ eV, photo-generated excitons should undergo very fast intra-band relaxation, on timescales of $\approx 3$ ps,\textsuperscript{18} and the low-lying exciton levels are promptly populated. The intra-band relaxation occurs via coupling to phonon modes, or heat, within the QW,\textsuperscript{18, 19} and the temperature of the system temporarily increases above room temperature.
4.3 Results & Discussion

The PL spectra from a single CdSe QW acquired at ten different power densities are plotted in Figure 4.1A. A log-log plot of the total integrated intensity for each PL spectrum included in Figure 4.1A reveals a linear dependence on power with a slope of 1.3, Figure 4.2. The shapes of and peaks within the PL spectra are observed to systematically and reproducibly change with increasing excitation power density, and we attribute these changes to emission contributions from different exciton levels with the charge carriers in the lowest valence and conduction bands. A simple analysis of the spectra indicate that the energies of the maximum intensities are found to be near one of three different values, 1.784, 1.790, and 1.830 eV, for this QW (Figure 4.1 B). The PL spectra acquired with the three lowest excitation power densities each have a maximum at 1.790 eV. As mentioned, internal conversion relaxes the photo-generated electrons and holes to the lowest electronic states in the conduction and valence bands, presumably the $1\Sigma_e$ and $1\Sigma_h$ states and the lowest 1-D exciton level, $n = 1$. The electronic notation used here ignores mixing of nearby electronic states, which may be particular prevalent in the valence band. In Chapter 3 of this work, photogenerated electron hole pairs in CdSe QWs were determined to be bound at room temperature. An estimate of the density of excitons within the QW indicates there is on average less than one exciton within the irradiation and detection region of the QW at any moment in time. Consequently, the observed emission is attributed to radiative recombination of bound, non-interacting electron-hole pairs in the lowest, $n = 1$ level.
Figure 4.1 Power-dependent PL spectral data. A) Normalized PL spectra from a single CdSe QW recorded using cw excitation at 2.33 eV (532 nm) are plotted and are offset for clarity. The excitation power density is listed on the left side and the estimated steady-state exciton population prepared within the ≈400-nm diffraction-limited spatial region on the QW is on the right in units of excitons cm\(^{-1}\). The energies of the lowest 1-D exciton level, \(n = 1\), the perturbed level, \((n = 1)^*\), and the first-excited exciton level, \(n = 2\), are labeled. B) The energies of the PL intensity maxima are plotted as a function of power density on a log scale. C) Gaussians centers obtained by fitting the PL spectra are plotted as a function of excitation power density on a log scale.
Each of the spectra acquired using the four next higher excitation densities has a maximum PL intensity that is shifted by $\approx 6$ meV to lower emission energy and an additional shoulder to higher energy than the $n = 1$ component. With power densities $\geq 1.2 \text{ kW cm}^{-2}$; we are preparing $2.46 \times 10^{26}$ excitons sec$^{-1}$ cm$^{-3}$ (more information about the exciton density calculation can be found in Appendix A). With increasing exciton densities, a Stark shift of the exciton levels may result from the electrostatic interactions between the excitons.\textsuperscript{22-25} In addition, the higher irradiation densities will result in an increase in temperature within the QW, and the higher temperatures will also shift the spectra to lower energy.\textsuperscript{26} Since the excitation photon energy is 2.33 eV and the $n = 1$ exciton level has an energy of 1.79 eV, approximately 0.54 eV of energy promptly converts into heat for each photon absorbed. The excitation power density of 1.2 kW cm$^{-2}$ corresponds to $\approx 0.7$ nW of power imparted to the QW within the excitation region. We conclude that the emission observed at these intermediate power densities is still attributed to radiative recombination of bound 1-D excitons in the $n = 1$ level of the $1\Sigma_e$ and $1\Sigma_h$ states, but the emission energy is shifted because both exciton-exciton
interactions and an increase in temperature within the CdSe QWs.\textsuperscript{26,27} We label this perturbed level as \( n = 1 \).

The maxima of the PL spectra acquired with excitation power densities \( \geq 5.0 \text{ kW cm}^{-2} \) is \( \approx 1.83 \text{ eV} \). At an excitation density of \( 40 \text{ kW cm}^{-2} \), as many as \( 8.18 \times 10^{26} \) excitons sec\(^{-1}\) cm\(^{-3}\) are generated, and 22 nW is imparted to the QW as heat near the irradiation region. The combination of the increased exciton density, the higher temperatures, and the shift to significantly higher energies suggest that this high-energy peak is associated with radiative recombination of excitons in the excited, \( n = 2 \) level of the ground \( 1\Sigma_e \) and \( 1\Sigma_h \) states. Even higher excitation power densities were used, but the QWs tended to melt, becoming amorphous pools of non-emitting materials, under these conditions. Since the melting temperature of bulk CdSe is 1500 K and that of 3.8 nm diameter CdSe QDs is reported to be 920 K,\textsuperscript{28} the melting point of the CdSe QWs should be intermediate between these values. For an excitation power density of 50 kW cm\(^{-2}\), up to 29 nW of heat is imparted to the QW, and its temperature is presumed to rise to near 1200 K.

A more thorough analysis of the power-dependent data was performed by fitting the PL spectra to multiple Gaussian peaks supports these assignments. Additional information about the fittings can be found in Appendix A. The spectra recorded with 0.80, 1.2, and 3.2 kW cm\(^{-2}\) fit well using two Gaussians. The intensity of the higher-energy Gaussian in each fit increases, but the center remains at \( \approx 1.835 \text{ eV} \) with increasing excitation densities, as shown in Figure 4.1 C. This peak is assigned to emission from the \( n = 1 \) level. The intensity of the lower-energy Gaussian also increases, but its center shifts to lower emission energies with higher excitation densities (solid purple squares). Again, the monotonic shifting of this emission component with excitation density is
attributed to the interaction of excitons in the ground, \( n = 1 \) exciton level and higher temperatures within the QW.

**Figure 4.3** A) – D) PL spectra of the same QW in Figure 1 at the indicated power densities (black) fit with three Gaussians (red). The three Gaussian peaks shown are referred to as the low-energy feature (magenta), the high-energy feature (cyan), and the broad feature (blue) in the text. Log-log plots of the integrated intensity of the broad feature E) and the high-energy feature F) against that of the low-energy feature.
A sum of three Gaussians, as shown in Figure 4.3 A - D, must be used to satisfactorily fit the four PL spectra recorded using the highest power densities from Figure 4.1. Two of the Gaussians are narrow, one at higher and one at lower emission energies, and the third is broader with a center energy lying between the other two. The lower-energy Gaussian is again attributed to \((n = 1)^*\) emission, and its center continues to shift with increasing excitation densities, down to 1.754 eV at 40 kW cm\(^{-2}\), as shown as the solid red squares in Figure 1 C. This shift is more than 0.036 eV to lower energy than that of the \(n = 1\) peak recorded at the lowest excitation powers. The maximum of the higher-energy feature remains near \(\approx 1.835\) eV for all power densities, open red squares. The integrated intensities of the broad and higher-energy Gaussians grow super-linearly compared to the low-energy Gaussian with slopes of 1.9(1) and 1.6(1), respectively Figure 4.3 E and F. Nearly identical trends were measured for other QWs, and the observed changes are reproducible and cannot be attributed to instabilities in the QWs since the spectra of a QW recorded at a given power density do not vary with time (Appendix A, Figure A.1).
Figure 4.4. Temperature dependence of exciton level energy. The maxima of the PL spectra recorded as a function of temperature and low excitation density are shown as open black circles. It is assumed that the emission is from the $n = 1$ exciton level. The centers of the lower-energy Gaussians obtained by fitting the power-dependent PL spectra to multiple Gaussians are shown as squares. These data are the same as shown in Figure 4.1C. In order to plot the Gaussian centers on a temperature scale, the temperature of the QW was assumed to be 295 K at an excitation power density of 500 W cm$^{-2}$. The temperature is assumed to scale linearly with excitation power density up to 50 kW cm$^{-2}$, at which the QWs were observed to melt. This temperature is assumed to be 1200 K, as described in the text.

In order to investigate the possible role of the increased temperature within the QW on the energetics of the emitting exciton levels, PL spectra were recorded as a function of temperature over the range of 295 to 395 K. For these studies, and excitation power density of 40 W cm$^{-2}$ was used so that only emission from the $n = 1$ level was observed at room temperature. The temperature-dependent data for one CdSe QW is
shown in Figure 4.4, open black circles. The maximum in each PL spectrum is observed to shift to lower energy with increasing temperature. For comparison, the centers of the low-energy Gaussians obtained when fitting the power-dependent PL spectra are also included. For these data, the temperature scale was approximated by assuming that the temperature of the sample at a power density of 500 W cm$^{-2}$ was 295 K. With higher power densities the temperature is assumed to scale linearly up to 50 kW cm$^{-2}$, at which power density the QWs would melt. As state previously, the melting point of bulk CdSe was measured to be 1500 K and that of 3.8 nm diameter CdSe QDs was measured to be 920 K.\textsuperscript{28}

In order to gain a general comparison, a power density of 40 kW cm$^{-2}$ was set to be 1200 K. Overall, the trend of a shift to decreasing emission energy of the \((n = 1)^*\) level with increasing excitation power density follows the temperature dependence of the \(n = 1\) peak. The \((n = 1)^*\) level may be shifted to even lower energies, but that may be due to exciton-exciton interactions. Unfortunately, the cryostat used for controlling the sample temperature could not be used to access higher temperatures, and the melting temperature could not be achieved.
With photoexcitation well above the band-gap energy of CdSe QWs, excitons quickly relax down to the low-lying exciton levels associated with the lowest $1\Sigma_h$ and $1\Sigma_e$ electronic states of the valence and conduction bands. At the lowest power densities, $\leq0.5$ kW cm$^{-2}$, emission is observed from the recombination of excitons in the singly-occupied, $n = 1$ 1-D exciton level. With power densities between 0.8 and 3.2 kW cm$^{-2}$, the exciton density becomes sufficiently high that excitons interact, and a shift to lower energy results. This perturbation of this ($n = 1)^*$ level depends on the exciton density, and continues to increase with irradiation, and thus exciton density. For power densities $>5.0$ kW cm$^{-2}$, the lowest state is largely occupied and the temperature within the QW is sufficiently high that additional photo-generated excitons occupy the next-higher excited-exciton level, $n = 2$.

Figure 4.5 Schematic of emitting 1-D exciton levels. With photoexcitation well above the band-gap energy of CdSe QWs, excitons quickly relax down to the low-lying exciton levels associated with the lowest $1\Sigma_h$ and $1\Sigma_e$ electronic states of the valence and conduction bands. At the lowest power densities, $\leq0.5$ kW cm$^{-2}$, emission is observed from the recombination of excitons in the singly-occupied, $n = 1$ 1-D exciton level. With power densities between 0.8 and 3.2 kW cm$^{-2}$, the exciton density becomes sufficiently high that excitons interact, and a shift to lower energy results. This perturbation of this ($n = 1)^*$ level depends on the exciton density, and continues to increase with irradiation, and thus exciton density. For power densities $>5.0$ kW cm$^{-2}$, the lowest state is largely occupied and the temperature within the QW is sufficiently high that additional photo-generated excitons occupy the next-higher excited-exciton level, $n = 2$.

A schematic of the exciton energy levels attributed to the emission peaks is included in Figure 4.5. At the lowest excitation power densities, a steady state of excitons is not achieved, and there is little heating of the QW. The photo-generated excitons promptly relax to the lowest exciton level, $n = 1$ with $1\Sigma_e$ and $1\Sigma_h$. These excitons radiatively recombine with emission energies close to that of the band-gap energy of the CdSe QW. With higher excitation power densities, both the number of excitons and the temperature of the QW increase. Once a steady-state of excitons is achieved, the interaction between excitons and the slight increase in temperature results in a shift to lower energy. At the highest excitation power densities, the combination of the large exciton densities and the high temperatures permits population to be found in the next higher exciton level, $n = 2$. The emission from these states should be sequential, with excitons in the $n = 2$ level preferentially emitting first, followed by those in the
perturbed \((n = 1)^*\) level, and finally by those in the \(n = 1\) level as the exciton density and temperature within the QW decreases with time.

Time-resolved PL data were acquired at different excitation energy densities to corroborate the assignments of the \(n = 1, (n = 1)^*\), and \(n = 2\) emission features. More details about time-resolved data can be found in Appendix A. The PL spectrum obtained using femtosecond-pulsed excitation with an energy density of 35 \(\mu\)J cm\(^{-2}\), Figure 4.6 A, is similar to the PL spectra recorded with \(cw\) excitation at low power densities, and contains emission from the lowest \(n = 1\) level, which is near 1.848 meV for this particular CdSe QW. For an energy density of 35 \(\mu\)J cm\(^{-2}\), we estimate that \(\approx 0.72 \times 10^{18} \text{ cm}^{-3}\) excitons are generated within the QW. When exciting with 176 \(\mu\)J cm\(^{-2}\), or generating \(\approx 3.6 \times 10^{18} \text{ excitons cm}^{-3}\), the maximum PL intensity is observed at nearly the same energy as the \(n = 1\) feature, although the PL feature is slightly broadened to both lower and higher energies. Using 559 \(\mu\)J cm\(^{-2}\), \(\approx 11.4 \times 10^{18} \text{ excitons cm}^{-3}\) are generated within the QW, and the time-integrated PL spectrum has a maximum intensity shifted by nearly \(\approx 40 \text{ meV}\) to higher energy than the maximum of the \(n = 1\) feature. At these excitation densities, it is presumed the emission occurs from the \(n = 1, (n = 1)^*\), and \(n = 2\) levels.
Figure 4.6 PL spectra and decay profiles. A) Time-integrated spectra from a single CdSe QW excited with ≈150 fs pulsed excitation at 559 μJ cm\(^{-2}\) (∙), 176 μJ cm\(^{-2}\) (◇), and 35 μJ cm\(^{-2}\) (□). The spectra are normalized by multiplying the 35 μJ cm\(^{-2}\) spectrum by ≈40 and the 176 μJ cm\(^{-2}\) spectrum by ≈5 and are offset for clarity.

B) Spectrally-resolved PL decays at different excitation intensities. The PL is detected at 1.878 eV with 26 meV resolution, and the same symbols are used as in A) to denote the excitation densities. C) The extracted (n = 1)* (◇) and n = 2 (∙) decay profiles as discussed in the text. The lines are single-exponential fits to the data with the indicated lifetimes.

Spectrally-resolved PL intensity decay profiles measured using a low-excitation density, 35 μJ cm\(^{-2}\), are nearly uniform across the PL spectrum with lifetimes measured to be ≈800 ps, blue squares in Figure 4.6 B. This uniformity suggests the emission is only from the n =1 1-D exciton level, and that no emission from trap states is detected. The PL intensity decay profiles recorded at 1.878 eV and with 176 and 559 μJ cm\(^{-2}\)
energy densities are also plotted in Figure 4.6 B as purple diamonds and red ×’s, respectively. The faster PL decay rates measured at higher excitation densities are indicative of a small contribution from non-radiative, Auger recombination of excitons in the \((n = 1)^*\) and \(n = 2\) levels. It is also possible that the rate for radiative recombination could be higher for the excited exciton levels, as was observed for CdSe QDs.\(^6\)

Since the decay profiles measured using the lowest excitation density, 35 \(\mu\)J cm\(^{-2}\), have no spectral dependence, these are assumed to represent the population decay of excitons in the \(n = 1\) level with contributions from all non-radiative pathways. The RT \(n = 1\) lifetime for these CdSe QWs is estimated to be \(800 \pm 60\) ps when exciting at 3.07 eV, and was obtained by averaging the single-exponential decay constants for numerous QWs. At slightly higher excitation density, 176 \(\mu\)J cm\(^{-2}\), the emission at 1.796 eV has contributions from both the \(n = 1\) and perturbed \((n = 1)^*\) levels. The PL intensity decay associated with the \((n = 1)^*\) level was obtained by scaling and subtracting the decay profiles measured at 1.796 eV with 176 \(\mu\)J cm\(^{-2}\) and with 35 \(\mu\)J cm\(^{-2}\). The extracted \((n = 1)^*\) decay profile for one QW is shown on a semi-log plot in Figure 4.6 C as purple diamonds, and is best fit with a single-exponential lifetime of 320 ps. Measurements on numerous QWs yield a \((n = 1)^*\) decay lifetime of \(350 \pm 40\) ps for an excitation density of 176 \(\mu\)J cm\(^{-2}\) at 3.07 eV.

Since the PL spectrum at an excitation density of 559 \(\mu\)J cm\(^{-2}\) is dominated by emission from the \(n = 2\) state, the decay profile associated with the \(n = 2\) state was estimated by scaling and subtracting the profiles obtained at 1.796 eV with 176 \(\mu\)J cm\(^{-2}\) and at 1.878 eV with 559 \(\mu\)J cm\(^{-2}\). The \(n = 2\) PL decay for a single QW is plotted in Figure 4.6 C as red ×’s, and is best fit with a single-exponential decay lifetime of 230 ps. The mean \(n = 2\) lifetime is \(200 \pm 40\) ps for an excitation density of 559 \(\mu\)J cm\(^{-2}\) at 3.07
eV. A further reduction in the \( n = 2 \) lifetime is observed when using even higher excitation densities, which is attributed to an increase in the contribution from Auger relaxation with the corresponding increase in exciton densities.\(^{18}\) Even though the exciton densities within the QW are quite high when using the highest \( cw \) and pulsed excitation densities, the observation of emission from an excited exciton level, \( n = 2 \), indicates that Auger interactions in QWs are not as strong as those in three-dimensionally confined colloidal QDs. Instead, such spectral features are usually resolved using gating techniques that capture transient spectra at short times after excitation when the average electron-hole pair population per QD is still appreciable.\(^{5,12,29-32}\)

Lastly, the spectral shift of the \( n = 1 \) feature from the \( n = 2 \) feature, 43-50 meV, enables the exciton binding energy to be estimated as 57 - 64 meV for these 10 nm CdSe QWs. This estimate was obtained using a simple hydrogen-atom model, where the energy of each exciton level follows \( E_n = -E_b/n^2 \). This binding energy is associated with the Coulombic interaction and the \( \phi \) component of the 1-D exciton. This large binding energy is consistent with those of 1-D semiconductor QRs, for which a binding energy of tens of meV is estimated.\(^{33}\) The corresponding exciton energy level is illustrated in Figure 4.7. The energies of the \( n = 1 \) and \( n = 2 \) levels are those observed experimentally. The difference in the two energies was used to solve for the exciton binding energy, \( E_b \). Although this model predicts the \( n = 3 \) level would be bound, sufficiently high exciton densities and temperatures could not be achieved to observe emission from this level. The energy shift attributed to quantum confinement of the electrons and holes can also be separated from the Coulombic component. The quantum confinement energy is \( \approx 120 \) meV for these 10 nm CdSe QWs.
Figure 4.7 Hydrogen-atom model of bound exciton levels. After photogeneration of excitons, prompt internal conversion lowers the energies of the excitons down to 1-D exciton levels associated within the lowest 1e and 1h electronic states of the conduction and valence bands. Emission from the $n = 1$ and $n = 2$ exciton levels are observed at the indicated energies. Using a simple hydrogen-atom model, the binding energy of the 1-D excitons is estimated to be $57 - 64$ meV, which yields the 1e – 1h asymptote. The $n = 3$ level was not observed, but should lie just below the exciton dissociation limit according to this model.

The ability to simultaneously prepare excitons in different 1-D exciton levels of a semiconductor QW at room temperature opens new possibilities for investigating exciton interactions and their dependence on dimensionality, as well as engineering of novel excitonic devices. Ongoing experiments are aimed at characterizing the ballistic nature, and thus the $e^z$ component of the quantum-mechanical wavefunction for 1-D excitons prepared in these CdSe QWs.
4.4 References


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Chapter 5

Delocalization of 1-D Excitons Over Entire CdSe Quantum Wires

5.1 Introduction

In an ideal semiconductor quantum wire (QW), the wave function of the electron-hole interaction along the length of the QW is unperturbed, and the probability of finding an exciton anywhere along the length of a perfect quantum wire is proportional to \( (e^{i k z})^2 \), which is constant. In real QWs, the density of trap sites largely dictates the photoluminescence quantum yield \( (\Phi_{\text{PL}}) \).\(^1\) Even so, with a lower dielectric constant of the surrounding medium relative to the semiconducting material, the exciton binding energy increases to the extent that electrons and holes can be bound as one-dimensional (1-D) excitons, even at room temperature, and these 1-D excitons then have a translational degree of freedom along the QW axis.\(^2\),\(^3\)

In recent work, it has been reported that CdSe QWs exhibit synchronous blinking along the entire length of the QW, with lengths greater than 5 μm.\(^1\) This blinking mechanism is attributed to a photolytic filling and emptying of surface traps. Photo-generated excitons can become trapped in long-lived surface-trap sites,\(^4\) and with continuous wave (cw) excitation, trap sites can eventually become occupied with excitons. As the trap sites become filled, the probability for radiative recombination of additional photogenerated excitons increases, and as a result, the \( \Phi_{\text{PL}} \) increases. Based on
this mechanism, it should be possible to photolytically fill trap sites, and modify the landscape of the QW such that the environment is suitable for 1-D exciton behavior along the length of the QW.

In this study, a new set of microscopy experiments are used to further probe the nature of 1-D excitons in single CdSe QWs. Using a cw wide-field (wf) illumination source, trap sites along the QW, presumably trap sites on the surface, are photolytically filled to create a near-perfect QW. The degree of delocalization and the nature of the 1-D wavefunction, $e^{i\kappa z}$, are interrogated by photo-generating additional excitons in a small region in the QW, and the change in PL intensity along the length of the QW attributed to these additional excitons is then measured.

5.2 Experimental

Exciton delocalization studies were performed following the procedure described in Chapters 2.3, optical microscopy, and 2.6, exciton delocalization. CdSe QWs were synthesized using the SLS-synthetic technique described in Chapter 2.1. The diameters of QWs used in this study were approximately 9 nm, with a PL peak for single wires centered at approximately 1.795 eV.
5.3 Results & Discussion

A schematic illustrating the photolytic filling of trap sites is shown in Figure 5.1. Using only diffraction-limited (dl) excitation ($\lambda_{\text{exc}} = 405 \text{ nm}$), photo-generated excitons are created at a specific position along the QW. As shown in this figure, they become localized in potential energy minima along the landscape of the QW (Figure 5.1 A), and therefore are prevented from delocalizing along the length of the QW. These potential minima are presumed to be deep, $> 30 \text{ meV}$, since this occurs at room temperature. Thus, when illuminating the QW with only the dl excitation source ($\lambda_{\text{exc}} = 405 \text{ nm}$), PL is only observed from the illuminated region of the QW (left end of the QW, Figure 5.1 A). A Lorentzian fit to the PL intensity versus position reveals that the FWHM ($\approx 450 \text{ nm}$) is roughly equal to the illumination spot size ($\approx 425 \text{ nm}$). Increasing the excitation fluence, and thus the number of photo-generated excitons, broadens the PL feature only slightly. This is because at higher excitation fluencies, the number of excitons generated increases, and non-radiative processes dominate due to exciton-exciton interactions. Thus, dl excitation alone will not suffice to fill all the traps in a QW. However, using wf excitation ($\lambda_{\text{exc}} = 488 \text{ nm}$), the entire QW is illuminated with a much lower power density, and excitons are photogenerated along the entire QW (Figure 5.1 B). Long-lived trap sites can become occupied with excitons, modifying the potential energy landscape of the QW felt by subsequently formed excitons. Photogenerated excitons from the second dl excitation source experience a modified potential energy landscape with fewer minima, and as a result, these excitons can delocalize along the length of the QW, and resemble 1-D quantum-mechanical particles in a cylinder. It is important to note that
when performing exciton delocalization experiments, the power density of the $dl$ excitation has to be low in order to observe delocalization. At high $dl$ powers, even with the modification of the potential energy landscape by $wf$ illumination, exciton delocalization is hindered by Auger relaxation from the high fluence of localized excitons (from $dl$ excitation).

![Figure 5.1](image)

Figure 5.1 Schematic of exciton delocalization experiments. A) Exciting the QW with only diffraction-limited excitation ($\lambda_{exc} = 405$ nm) generates excitons in a small part of the QW, and they become localized in trap sites near the excitation region. B) Illuminating the QW with wide-field excitation ($\lambda_{exc} = 488$ nm) photofills potential minima along the wire, thus creating favorable conditions for exciton delocalization.

To monitor the degree of delocalization of the excitons generated after $dl$ irradiation, a series of images were taken using wide-field excitation only (Figure 5.2 A),
both \textit{wf} and \textit{dl} excitation (Figure 5.2 B), and \textit{dl} excitation only (Figures 5.2 D and 5.2 F). Electronic shutters were placed in the paths of the \textit{wf} and \textit{dl} excitation sources to allow for quick switching of illumination light. Because CdSe QWs can exhibit intrawire fluctuations, images were recorded with an exposure time of just 100 ms. Typical power densities for the two excitation sources ranged from 50 – 500 W/cm$^2$ for wide-field excitation ($\lambda = 488$ nm), and 1 – 50 W/cm$^2$ for diffraction-limited excitation ($\lambda = 405$ nm). To analyze the data, the integrated PL intensity of the microscopy images are plotted as a function of position along the length of the QW, as shown in Figure 5.2 C. The PL traces are denoted as PL$_{\text{wf}}$ for the image obtained using only \textit{wf} illumination (blue trace, Figure 5.2 C), and PL$_{\text{both}}$ for the image obtained using both \textit{wf} and \textit{dl} excitation sources (red trace, Figure 5.2 C). Then, the PL intensity is plotted as a function of position for the image obtained using only \textit{dl} excitation (purple trace, Figure 5.2 E, denoted as PL$_{\text{dl}}$). In order to determine the PL intensity attributing to the diffraction-limited irradiation in PL$_{\text{both}}$ and thus the range over which these excitons diffuse, PL$_{\text{dl}}$ is compared to $\Delta$PL (black trace, Figure 2 E), where $\Delta$PL = PL$_{\text{both}}$ – PL$_{\text{wf}}$. A difference in PL between $\Delta$PL and PL$_{\text{dl}}$ is evidence for exciton delocalization. In the PL intensity versus position plots, all PL traces are normalized, and the position of the \textit{dl} illumination spot is centered at zero.
Figure 5.2  Exciton delocalization data for a single CdSe QW. PL microscopy images of a single CdSe QW are shown in A) and B), recorded using \(wf\) excitation only, and both \(wf\) and \(dl\) excitation, respectively. C) Plot of the intensity versus position corresponding to images A and B for \(wf\) excitation only (red trace) and both \(wf\) and \(dl\) excitation (blue trace). D) PL microscopy image using only \(dl\) excitation, exciting on the right end of the wire. E) Plot of the intensity versus position corresponding to image D (purple trace),
and ΔPL (black trace, where ΔPL = PL_{both} − PL_{wf}). F) PL microscopy image exciting on the other end of the wire using dl excitation only. (G) Plot of the intensity versus position corresponding to image F) (purple trace), and ΔPL (black trace).

Figure 5.2 includes exciton-delocalization data for a single QW. Figures 5.2 A and B are PL microscopy images of the QW using wf excitation, and both wf and dl excitation, respectively. The diffraction-limited illumination spot is approximately 425 nm in diameter, and is focused just on the right side of the QW, at position zero. Figure 5.2 C is a plot of the PL intensity versus position for wf excitation only (blue) and both wf and dl excitation (red). The PL intensity in each plot represents the integrated PL for the entire wire. Figure 5.2 D is a PL microscopy image of dl excitation only. In Figure 5.2 E, the black trace represents ΔPL, where ΔPL = PL_{both} − PL_{wf}. This represents the PL intensity from those excitons that have delocalized along the wire. Comparing this trace to the plot of the dl excitation only (Figure 5.2 E, purple trace), there is a change in PL along the entire length of the QW. Since the PL contribution from wf illumination has been subtracted, we attribute this change in PL to exciton delocalization.

Delocalization along the entire wire occurs within the exciton lifetime of approximately 1 ns. This is indicative of weak exciton-phonon coupling, which would shorten the exciton lifetimes and diffusion length. In Figure 5.2 E, ΔPL is positive towards the left of the illumination spot, but dips negative towards the ends of the QW. A proposed hypothesis for this behavior is as follows: the excitons diffuse along the QW, but the 1-D infinitely long nature of the QW is obviously not valid at the ends, and the exciton density increases at the ends. Auger relaxation will occur with the increased exciton density, resulting in decreased PL. For this QW, this behavior is also present if
the diffraction-limited illumination spot is moved to the left end of the QW (Figure 5.2 F). It is important to emphasize that even with a negative ΔPL, there is a change in PL that spans the entire distance of a 10 μm long QW. Most experiments result in a positive ΔPL along the QW, thus the 1-D excitons can be observed over an entire QW if the potential minima are filled.

Exciton delocalization has been observed previously in other quantum-confined systems. Arakawa and coworkers measured exciton diffusion lengths up to 4 μm for 1-D GaAs QWs at temperatures of 15 K. In 2-D ZnSe quantum wells, exciton delocalization was observed to span a few microns, performed at low temperature (7 K). Exciton diffusion lengths in 2-D AlAs/AlGaAs double quantum well structures measured up to 500 μm at a temperature of 1.8 K. Exciton diffusion lengths in 2-D InGaAs quantum wells was reported up to distances of microns, at slightly warmer temperatures of 90 K.

In the current study, exciton delocalization in single room-temperature CdSe QWs spanning up to 10 microns is reported. The mechanism in this study, where photogenerated excitons fill trap sites, modifying the potential-energy landscape along a QW that will dictate the diffusion and dynamics of excitons prepared within the QW, is similar to an exciton diffusion study reported in 2-D AlAs/AlGaAs double quantum wells. In that study, the authors claim that following the excitation pulse, a dipole-dipole repulsion between aligned excitons causes a drift-like motion. As excitons drift further from the excitation spot, they fill up trap sites, which allows other excitons to diffuse further. At later times, the exciton density drops, and pure exciton diffusion dominates.
The change in PL observed along the entire length of the QW does not necessarily indicate the delocalization of bound electron-hole pairs. Kuno and coworkers observed evidence for the presence of individual charge carriers in single CdSe QWs. However, more recent studies have indicated that bound electrons may exist in single 1-D CdSe QWs. To determine if bound excitons were responsible for the PL intensity changes observed in the current study, similar exciton delocalization experiments were performed in an electric field. If individual charge carriers are present, we would expect a change in the PL intensity that would depend on the direction of the electric field as the electrons or holes would be influenced by the field. In contrast, bound excitons are neutral, and an electric field should not have an effect on the PL intensity or exciton delocalization.

Figure 5.3 includes the results from delocalization experiments performed on a single CdSe QW in the presence of an external electric field. The strength of the external electric field was 3.25 kV/cm, exposure times for all images were 100 ms, and power densities were the same as listed above, approximately 50 - 500 W/cm² for \textit{wf} excitation, and 1 – 50 W/cm² for \textit{dl} excitation. The PL intensity image of a single CdSe QW is shown in Figure 5.3 A. The ΔPL profile obtained by subtracting PL\textsubscript{wf} from PL\textsubscript{both} is shown as the black trace in Figure 5.3 B. For comparison, the PL intensity profile obtained with only \textit{dl} excitation is shown as the purple trace.

With the electric field on (Figure 5.3 B), ΔPL (black trace) spans microns, and is somewhat evenly distributed, not favoring either end of the QW. With the electric field off (Figure 5.3 C), ΔPL (black trace) still spans the entire length of the QW, and is similar to ΔPL observed in the presence of an electric field. Such experiments indicate that exciton delocalization is due to bound electron-hole pairs, versus individual charge
carriers. It should be noted that although ΔPL is similar with both the electric field on and off, it is not identical. This is expected, because the potential energy landscape is constantly changing with the non-statistical filling and emptying of trap sites by wide-field illumination.

Figure 5.3 Exciton delocalization performed in the presence of an external electric field. A) PL microscopy image of a CdSe QW used in electric-field experiments, taken using w/ excitation only. A plot of the PL intensity as a function of position for ΔPL (black trace), and PL_{dl} (purple trace) with the electric field on (B), and the electric field off (C).
5.4 Conclusion

In conclusion, we observe 1-D exciton delocalization in single CdSe QWs, spanning distances up to 10 microns. The potential energy landscape becomes suitable for delocalization by photolytically filling trap sites in the QW using \( \textit{wf} \) illumination. Experiments performed in an electric field support the hypothesis that bound electron-hole pairs are responsible for delocalization and observed PL intensity changes, not individual charge carriers. The results in this study suggest that excitons in CdSe QWs can behave as 1-D quantum mechanical species, with an excitonic wavefunction that can span microns in length. Since the probability of finding an exciton is proportional to \( e^{2ikz} \) squared, the probability of finding an exciton anywhere along a QW is a constant.
5.5 References


Chapter 6

Low Temperature Spectroscopy of 1-D CdTe Quantum Wires

6.1 Introduction

One-dimensional (1-D) semiconductor quantum wires (QWs) are a unique class of nanomaterials. They can be synthesized with small diameters to give rise to quantum confinement effects, and thus their optical electronic spectra can be tuned by varying the diameter of the wire.\textsuperscript{1-3} Their lengths make them attractive candidates for implementation into photovoltaic solar cells and opto-electronics because they can, in principle, transport charge efficiently across large distances. Unfortunately, reported photoluminescence quantum yields ($\Phi_{\text{PL}}$) are low for CdSe QWs,\textsuperscript{4,5} though preliminary studies on CdTe QWs have indicated a $\Phi_{\text{PL}}$ of 5%.

The dynamics of charge carriers and the photoluminescence (PL) properties of semiconductor nanostructures are incredibly sensitive to the conditions of the nanostructure surface. In semiconductor CdSe nanocrystals, adding a shell to the nanocrystal surface modifies the electronic structure of the nanocrystal by passivating non-radiative trap sites on the surface of the dot. As a result, a significant increase in PL is observed.\textsuperscript{6-9} Likewise, Mews and co-workers added a CdS shell to CdSe nanowires and increased the $\Phi_{\text{PL}}$ from 0.14% to as high as 0.46%.\textsuperscript{5} Modifying the surface of a nanostructure can affect the density and energetics of “surface traps”, which is a general
name for minima in the potential energy landscape that scatter or trap separate charge carriers or excitons. In a QW, the large surface area gives rise to a larger number of trap sites, in comparison to QDs, and the increase in the probability for non-radiative recombination tends to result in a significantly low $\Phi_{\text{PL}}$. The thermal energies of excitons or separate charge carriers prepared in the QWs in comparison to the depths of the potential minima will dictate the likelihood for these scattering or trapping events. For instance, at room temperature ($RT$), excitons have sufficient thermal energy ($k_B T$) to traverse shallow potential minima and the resultant exciton behavior may resemble that of a 1-D exciton sampling either an average potential or a mildly undulating potential energy landscape ($PEL$). At low temperatures, however, the smallest of variations in the $PEL$ will influence the dynamics of the photogenerated excitons. These excitons may become trapped in local potential minima, and either nonradiatively recombine or radiatively recombine with specific emission energies associated with the electronic energies of that specific trap site.

The 1-D behavior of excitons can only be achieved if the $PEL$ along the length of a QW is nearly uniform. Previous work from our group studied the $PEL$ of CdSe QWs at $LT$. Localized, discrete features in the PL spectra were observed for temperatures below 40 K. This indicates that there are traps or potential minima that are on the order of 3 meV. Most of the QWs studied had several discrete peaks in the low-temperature PL spectra, and these peaks are separated by less than 40 meV. By recording the PL spectra as a function of position along the length of a single CdSe QW, it was determined that these discrete peaks arise at different positions along the QW. These spectroscopic results suggest that there are at least two types of potential minima along CdSe QWs,
shallow minima superimposed on an undulating potential. At $RT$, the thermal energy lies above the 3 meV potential minima, but the low PL QYs suggest that a majority of photogenerated excitons do become trapped in these minima. It is possible, however, to fill or occupy some of these traps with photogenerated excitons and then observe the 1-D nature of excitons in these QWs.

In this chapter, the temperature-dependence of the PL spectra recorded for single CdTe QWs is reported in order to characterize the $PEL$ along the length of single CdTe QWs that may perturb the 1-D nature of the excitons. The PL spectrum is analyzed as a function of temperature, position along the wire, and time. Our data indicates that the $PEL$ within CdTe QWs changes as trap sites are continuously emptied and filled with photo-generated excitons, and that the potential along a single QW is not uniform. Localized features in single 1-D structures has been observed previously in GaAs wires,\textsuperscript{11} and in CdSe/ZnS quantum rods.\textsuperscript{12} Sharp, localized features in the PL spectra indicate that excitons become localized in potential energy minima within the wire. Additionally, we show that the PL intensity at $LT$ is an order of magnitude larger than at $RT$, presumably because excitons are not able to thermally access non-radiative recombination pathways.

6.2 Experimental

CdTe quantum wires with a diameter of approximately 7 nm were prepared using the SLS-technique developed by Buhro and co-workers,\textsuperscript{13} as described in Chapter 2.1. LT microscopy studies were performed on single CdTe QWs using procedures outlined
in Chapters 2.3 (optical microscopy) and 2.7 (low-temperature studies). Single CdTe QWs were excited using a 2.331 eV (532 nm) cw diode laser, which is 600 meV above the band-gap energy (1.73 eV) for these CdTe QWs. Since CdTe QWs are sensitive to air and rapidly photobleach, sample preparation was performed in a nitrogen glovebox. One to two drops of a dilute CdTe QW solution in toluene were drop-casted onto a quartz coverslip, placed into the helium cryostat, and immediately evacuated down to a pressure of 10^{-6} mTorr. Ensemble-emission experiments indicated that the $\Phi_{\text{PL}}$ for this particular sample was approximately 4%. The lengths of the CdTe QWs were in the range of 1 – 5 μm, as determined by optical microscopy experiments and TEM images.

### 6.3 Results and Discussion

The temperature dependence of the PL spectra recorded for a single CdTe QW is included in Figure 6.1. The PL spectra were obtained using 532 nm (2.331 eV) excitation with a power density of 200 W/cm². (Note that different integration times were used in recording the spectra, as evidenced by the varying signal-to-noise levels.) The PL intensity along the entire length of the QW was integrated to obtain the spectra. The samples were first cooled to 4 K, and the spectra were recorded as a function of increasing temperature. The $RT$ PL spectra of individual CdTe QWs have a single peak centered at approximately 1.725 eV, as shown in Figure 6.1, magenta spectrum. The spectral shift of this PL feature from the $RT$ band-gap energy of bulk CdTe, 1.56 eV, indicates that these QWs have sufficiently small diameters for quantum-confinement in
The PL-intensity profile of the RT spectrum fits well to a Lorentzian, with a fairly narrow linewidth of 54 meV. Noticeably narrower, discrete PL features become observable, and the overall intensity of the PL spectrum increases significantly with decreasing temperature. In general, the discrete features are present for temperatures below 100 K.

This trend of observing discrete features with decreasing temperature is similar to that observed for CdSe QWs, although the discrete features were observed for sample temperatures below 40 K for CdSe QWs. What was not observed for the CdSe QWs, however, was a shifting of the PL features to higher energy with decreasing temperature. The peaks in the CdTe QW PL spectra shift from 1.725 eV to 1.8 eV when going from 300 K to 4 K, as shown in Figure 6.1. A shift in the band-gap energy towards larger energies with decreasing temperature is often observed for bulk semiconductor materials, and is often characterized using the Varshni relationship, \( E_g = E_0 - \alpha T^2/(T+\beta) \), where \( \alpha \) and \( \beta \) are material constants, with \( \beta \) related to the Debye temperature (140 K for bulk CdTe), and \( E_0 \) is the band-gap at low temperature (1.8 eV, from our experimental data). According to the Varshni relationship, a shift in the band-gap energy of approximately 90 meV would be predicted for CdTe. Although this value does not agree with the experimental value (75 meV), the general trend of increasing \( E_g \) with decreasing temperature is observed.
In the temperature-dependent study included in Figure 6.1, the PL spectrum recorded at 4 K (black) was recorded first. The 4 K- PL spectrum contains several discrete peaks in the low-energy region and a more intense and broader peak centered at 1.83 eV. As the temperature of the sample is increased the PL features shift to lower energies, and the discrete, narrow peaks broaden into a single feature. For temperatures above ≈ 100 K, no narrow discrete features are observed. For this specific CdTe QW, two broad features are still present, but this is not always observed. These two features merge into a single peak at temperatures above 200 K, which can be fit well to a single Lorentzian. The maximum intensity observed in the PL spectra shifts by a total of 75 meV to lower energy in going from 4 K to 300 K.
Not only is the *PEL* of a wire continuously modified as excitons are photo-generated, but the landscape along the length of a QW is also not uniform. Analyzing PL spectra as a function of position illustrates this, as shown in Figure 6.2. This is a PL spectrum of a single CdTe QW at 4 K. The four different traces in the plot represent spectra at different positions along the length of a QW. The inset in the graph is the PL microscopy image of the wire, and the boxes are color coded to correspond with their respective PL spectra. The PL profile at the top of the wire (red trace) is much different than the PL profile from the bottom of the wire (green trace). At the top of the wire, there are three distinct, narrow features at 1.805 eV, 1.790 eV, and 1.760 eV. At the bottom of the wire, the emission shape is different, with two distinct peaks at 1.775 eV and 1.805 eV, and a slight shoulder at 1.790 eV. PL features in the middle of the wire also have some unique features, such as the sharp peak at 1.755 eV in position 3 (orange trace). Although, the PL peaks in position 2 (blue trace) are the same as position 1 (red trace), but with a different relative intensities. Even so, it is clear from this figure that the potential landscape is not uniform along the entire length of the wire.
Figure 6.2 PL spectra as a function of position along the length of a single CdTe QW at 4 K.

The localized features observed in the LT single CdTe QW PL spectra most likely result from variations of the dimensionality and crystal structure along the length of the QW. The PL spectra acquired at different positions along a single CdTe QW, Figure 6.2, indicate that the spectra definitely change as a function of position, and these variations may likely occur on spatial scales that are small in comparison to the optical-detection resolution of the microscope, 800 nm. High-resolution transmission-electron microscopy (HR-TEM) images, Figure 6.3, indicate there are zinc blende (ZB) and wurtzite (W) segments along the length of the QW. The difference in the ZB and W band-gap energies is approximately 47 meV, but the offsets are such that a type-II heterostructure results
with the VB and CB energies of the W domains lying 18 and 65 meV to higher energy than those of the ZB domains.\textsuperscript{17} Because of these domains, emission might occur over a range of energies spanning up to 65 meV. The precise lengths of each domain varies between synthesis batches, and also to a lesser degree within a single synthetic batch.\textsuperscript{13, 18} The CdTe QWs in this batch have average ZB and W segment lengths of 5.6 and 1.1 nm, respectively. Most of these segment lengths are less than the approximate Bohr radius of a 1-D exciton in CdTe, 7.3 nm,\textsuperscript{19} and as a result, any photogenerated excitons within a typical CdTe QW will sample an average potential dictated by the VB and CB offsets weighted by the lengths of the ZB and W domains.

Mews and co-workers showed that due to the short lengths of the domains in CdSe QWs there is little localization of electrons and holes in the domain regions, and indeed the average energies are experienced and there are only small shifts in the VB and CB states.\textsuperscript{18} We expect a similar behavior for the CdTe QWs. In addition, the electron-hole binding energy is expected to be on the order of the difference in the ZB and W band-gap energies. If the exciton binding energy is greater than 65 meV, the excitons will remain bound, and a further averaging of the adjacent domain energies will be experienced. Additional changes in energy may result from slight variations of the diameters in the adjacent domains. A last consideration in the energetics of that would be experienced by excitons in the CdTe QWs has to do with surface passivation of the QWs. It is expected that the interface between domain regions may have the highest propensity for defects, and due to the abrupt change in structure, surface bonds at the interface regions may be difficult to chemically passivate. The degree of passivation can
not only be associated with the presence of surface trap sites, but it will also give rise to subtle changes in the shapes of the \textit{PEL} that are largely dictated by the heterostructure.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6_3.png}
\caption{HR-TEM image of CdTe QWs (courtesy of Dr Fudong Wang from the Buhro group).}
\end{figure}

The presence of localized features at low temperatures is illustrated using the schematic in Figure 6.4. Upon \textit{w}f illumination, photo-generated excitons can localize into trap sites within the QW. Excitons can either nonradiatively recombine, or radiatively recombine with specific PL energies that are associated with the energies of that specific trap. Potential minima in QWs are presumed to arise from surface irregularities, lattice defects (as described above), or phase admixtures.\textsuperscript{4} The role the \textit{PEL} plays in the PL properties of QWs is consistent with studies performed on QDs, where surface chemistry is a determining factor in the PL properties.\textsuperscript{20-22}
Figure 6.4 A schematic illustrating the cause of localized PL features in a QW at low temperatures. Upon wide-field illumination, excitons can become stuck in potential minima at low temperatures. Recombination from these trap sites gives rise to localized, discrete features in the PL spectrum.

In addition to a shift in band-gap energy, and the presence of localized, discrete features, cooling down to LT results in a PL enhancement. Figure 6.5 is PL spectra of a single CdTe QW taken at 4 K (black), and at 300 K (magenta). The integrated PL intensity of the entire spectrum at 4 K is a factor of approximately 50 higher than the integrated PL intensity at 300 K. This increase in PL is presumed to be due to the decrease in thermal energy, which reduces the thermal population down to the lowest excitonic levels, and reduces broadening from phonon-related broadening mechanisms. An increase in PL with decreasing temperature has been previously observed in CdSe QDs. At lower temperatures, there is less contribution to phonon modes, a route for
nonradiative recombination. Additionally, excitons have less thermal energy to populate potential non-radiative surface trap sites.

Figure 6.5 Emission spectra of a single CdTe QW at 4 K (black trace) and 220 K (red trace).

The PL spectra associated with a specific temperature are sometimes observed to change after cycling from low temperature (4 K) to high temperature (RT) while irradiating. The initial PL spectrum of a single CdTe QW at 4 K is shown in Figure 6.6, black. This is the same 4 K spectrum shown in Figure 6.1 and 6.4. After cycling up to RT and then back down to 4 K, the purple spectrum was recorded at 4 K. The total elapsed time between recording the two spectra was approximately one hour. The PL
intensities are normalized to illustrate a clear comparison of the PL features of the two wires. In this figure, the emission spectrum of a single wire was taken at 4 K (black trace), then the QW was warmed to RT while taking temperature-dependent PL spectra. The temperature was then returned back down to 4 K (purple trace). It is clear from this plot of the two PL traces that the potential energy landscape of the wire has changed, since the PL features are not identical. During the temperature-dependence experiment, the QW is illuminated with \textit{cw} excitation light for a significant period of time (in this case approximately 1 hour), and photo-generated excitons are continuously emptying and filling trap sites in a wire. This idea of continuously modifying the potential energy landscape is consistent with previous CdSe QW blinking data,\textsuperscript{25,26} and delocalization along the length of CdSe QWs (Chapter 5).
In conclusion, at low temperatures (4 K), excitons can become stuck in potential energy minima along the landscape of a QW, which gives rise to the narrow, localized PL features. The band gap shifts to higher energies at LT, in accordance with the Varshni relationship, which describes the change in the energy gap of semiconductors with temperature.\textsuperscript{15} We hypothesize that PL at LT originates from trap sites that are below the band gap. The potential energy landscape of a single QW is not uniform, as evidenced by
analyzing PL spectra as a function of position along the length of a wire. Additionally, the PL intensity increases at LT by a factor of approximately 50. This increase in intensity is presumed to be due to thermally reducing the population down to the lowest exciton levels, which decreases the likelihood for excitons to encounter non-radiative recombination pathways.
6.5 References


Chapter 7

Optical Properties and Spectroscopy of Single CdSe Quantum Belts

[Portions of this chapter have been published as


7.1 Introduction

Semiconductor quantum belts (QBs) are one-dimensional (1-D) structures with a confined thickness dimension, a weakly confined width dimension, and an elongated length (Figure 7.1). Typically, colloidally-synthesized QBs are 1.5 – 2 nm thick, 7 – 15 nm wide, and 0.5 – 1.5 μm long.\(^1\) Their structure is similar to CdSe nanoribbons synthesized by Hyeon and coworkers.\(^2\) With strong quantum confinement in the thickness dimension, and weak confinement in the width dimension, QBs, in theory, have a tunable band gap energy, analogous to 1-D particle in a box behavior. However, despite significant efforts, synthetic control by the Buhro group of the thickness dimension has been unsuccessful, as the only thicknesses obtained were either 1.5 or 2 nm.
Figure 7.1. Schematic of the shape of a quantum belt.

7.2 Experimental

CdSe QBs with photoluminescence (PL) quantum yields (QYs) of up to 30% have been synthesized by the Buhro group\textsuperscript{1} using a method similar to that of Peng and co-workers.\textsuperscript{3} Briefly, a Schlenk flask under dry N\textsubscript{2} containing 72 mg of Cd(OAc).H\textsubscript{2}O (cadmium acetate) and 6.3 g of n-OA (n-octylamine) was placed in an oil bath at 65\textdegree{}C for 1 hour with stirring. In an air-tight vial, a solution of 58 mg of selenourea in 1.35 g of n-octylamine was sonicated for 10 - 15 minutes to dissolve the selenourea, and immediately injected into the Schlenk flask. A color change of colorless to yellow, orange, and finally greenish yellow (after 3 – 4 hours) was accompanied by the reaction. The solution was stirred for 18 – 24 hours at 63 – 68 \textdegree{}C, and then at 90 – 110 \textdegree{}C for 1 hour. The ending solution was a greenish-yellow color.\textsuperscript{1}

Single QB PL spectroscopy measurements were conducted using epi-fluorescence optical microscopy techniques, as described in Chapter 2.3. Argon gas was streamed
over the sample during microscopy experiments to help reduce the effects of photobleaching, which will be discussed later in this work. A 3.061 eV (405 nm) cw diode laser was used to excite the QBs, and typical power densities ranged from 5 - 150 W/cm$^2$. Ensemble absorption and emission measurements were taken using the procedure described in Chapter 2.2.

7.3 Results & Discussion

The room-temperature extinction spectrum of an ensemble sample of QBs suspended in toluene is shown in Figure 7.2. This spectrum contains two distinctive absorption peaks at 2.77 and 2.95 eV, and a broad peak around 3.3 eV. These three features are assigned to the $1_B - 1_e$ (2.77 eV), $1_A - 1_e$ (2.95 eV), and $2_B - 2_e$ transitions ($B$ = heavy hole, $A$ = light hole, and $e$ = electron), analogous to those transitions for CdSe nanoplatelets assigned by Dubertret and coworkers. The energies of the absorption features in the spectrum can be fit to a simple effective-mass-approximation, particle-in-a-box (EMA-PIB) model, as shown in equation 1.

\[ \text{(1)} \]
In this equation, $E_g$ is the band gap energy of wurtize bulk CdSe (1.751), $h$ is Planck’s constant, $n$ is the quantum number, $t$ is the belt thickness, is the electron effective mass (0.12), is the hole effective mass ($\mu_0 = 0.90$, $\mu_5 = 0.45$), is the bulk exciton binding energy (14.8 meV), and is the free electron mass.

Using the EMA-PIB model, the $1_{\text{hh}} - 1_{\text{e}}$ was calculated to be 2.79 eV, and $1_{\text{lh}} - 1_{\text{e}}$ was calculated to be 2.95 eV, which matches well to the ensemble extinction spectrum shown in Figure 7.2. The energy calculated for the $2_{\text{hh}} - 2_{\text{e}}$ transition was 6.08 eV, and did not match up well with the experimental data from the extinction spectrum (Figure 7.2). The EMA-PIB model fits well to lower energy transitions, but breaks down at higher energy transitions because it assumes isotropic bands, parabolic band shapes, and infinite-potential barriers, and uses bulk values for the electron and hole effective masses. The fact that QBs fit well to EMA-PIB model, and are similar to structures previously reported for CdSe nanoribbons, nanoplatelets, and nanosheets, establishes that they exhibit behavior of 1-D quantum confined systems.
Figure 7.2. Ensemble extinction (black) and emission (red) spectra from CdSe QBs.

Figure 7.2 also includes a PL spectrum recorded at room temperature of CdSe QBs suspended in toluene. The PL feature is Stokes shifted from the lowest-energy absorption feature by approximately 25 meV, and is extremely narrow. A FWHM fit to the emission curve is equal to 50 meV. In comparison, 1-D CdSe quantum wires, with diameters of approximately 10 nm have a FWHM of approximately 110 meV.

Upon exposure to cw irradiation, 405 nm with a power density of 100 W/cm², the PL intensity of single QBs rapidly decreased. As shown in Figure 7.3, this PL decay typically occurs on timescales less than 50 – 100 seconds, and it is believed to result from the photooxidation of the CdSe surface, most likely at the edge of the QBs. Surface traps form that increase the rate of non-radiative recombination and a decrease in the observed
PL intensity. By purging the sample with a stream of Ar gas, the PL intensity at the QBs remained more stable, lasting up to a few hours.

Figure 7.3. PL intensity versus time of a single CdSe QB recorded under ambient conditions.

Photooxidation of CdSe nanocrystals has been studied previously. The rate of photobleaching for CdSe QDs and CdSe/ZnS core/shell QDs was found to decrease by a factor of 4 when the samples were exposed to an inert nitrogen atmosphere. The PL intensity of QDs in air was initially more intense than the PL in N₂. This was reportedly caused by O₂ quenching of deep-trap emission. In a study conducted by Alivisatos and coworkers, Se surface sites in CdSe QDs were oxidized upon exposure to air, forming a
SeO₂ surface film, which causes nanocrystals to degrade over time.¹³ In CdSe cluster molecules, partially reversible photodarkening was observed, which was attributed to a temporary charging mechanism.¹⁴ The charging quenched the PL via an efficient, non-radiative Auger recombination.

Emission intermittency, commonly referred to as “blinking”, has been observed and is well documented in single CdSe and CdSe/ZnS QDs.¹¹,¹⁵-¹⁹ ²⁰-²² In the “on” state, photogenerated excitons radiatively recombine, and high PL intensities are observed. When in an “off” state, the QD is charged, and this charge gives rise to efficient nonradiative Auger recombination. This charging model,¹¹ however, has been recently challenged.²³-²⁶ By measuring the exciton PL intensity time traces of single CdSe/CdZnS core/shell QDs, Bawendi and coworkers determined that the dark-state PL QY is 10 times less than the biexciton PL QY.²³ These results strongly contradicted predictions of the charging model, where emission from charged exciton states and multi-exciton states were assumed to be quenched by nonradiative Auger recombination. Leone and coworkers measured the nonradiative recombination rate during the off-states of CdSe QDs.²⁵ They determined that the nonradiative rate depends on the duration of the off-state, with higher rates associated with longer off times. This suggests varying nonradiative processes, which contradicts charging models where a single nonradiative rate is predicted, regardless of off-state duration.²⁵ Blinking models that support a fluctuating trapping rate instead of long-lived charge carrier trap sites are gaining support.²⁷,²⁸ In these mechanisms, the particle remains bright as long as the charge trapping rate is slower than the fluorescence rate.
Rapid variations in the PL intensity, or blinking, are also observed in single CdSe QBs, as shown in Figure 7.4. This figure is a plot of the PL intensity versus time for 3 different QBs at room temperature. In this graph, the black trace represents a QB with a fairly consistent PL intensity. In contrast, the PL intensity is intermittent for the QB represented by the red trace. The QB blinks “off” at approximately 3 seconds, then returns to an on state after 10 seconds. The QB represented by the blue trace is either off or dim until approximately 15 seconds, where it quickly blinks on before returning to an off state. Although QBs can have lengths spanning up to 1.5 μm, thus behaving as 1-D quantum structures, blinking was much more pronounced in smaller QBs. However, we do not eliminate the possibility of blinking in longer QBs, as blinking in single 1-D CdSe QWs has been observed previously.29
Figure 7.4. PL Intensity versus time for 3 different QBs at room temperature. Data recorded under Argon atmosphere.

The emission spectra of single CdSe QBs were recorded at room temperature in an Ar atmosphere using 405 nm (3.061 eV) excitation with a power density of approximately 100 W/cm$^2$. Due to the detection resolution of the microscopy (0.4 – 0.6 μm), since the dimensions of the QBs are 1.5 nm x 7 nm x 1 μm, PL microscopy images of the QBs appear as slightly oblong structures as shown in Figure 7.5 A and B. The PL spectrum of ensemble CdSe QBs suspended in solution (black trace in Figure 7.5 C), has a maximum at 2.75 eV with a fairly narrow breadth of 50 meV. The PL spectra of single QBs have approximately the same energies, but are slightly narrower (Lorentzian FWHM = 48 ± 15 meV). The band-edge emission energy shifts slightly between QBs, and is
attributed to sample inhomogeneities. Emission from single QBs did not change significantly with increasing excitation intensity (2 – 500 W/cm²), although the PL began to photobleach rapidly at higher power densities as stated previously.
**Figure 7.5.** Emission and polarization data from single CdSe QBs. Wide-field PL microscopy image of A) several QBs, and B) a single QB. C) Emission spectra from single QBs (colored traces) and ensemble QBs (black). PL microscopy images of a single QB with an emission polarizer at D) $\theta = 180^\circ$, and E) $\theta = 90^\circ$. F) Emission intensities collected at various polarization angles for a single QB (black), fit to a $\cos^2 \theta$ dependence (red trace).
Figures 7.5 D-F represents polarization data recorded for a single QB. This data was taken using a UV-polarizer mounted to a mechanical rotation stage, positioned in front of the entrance-slit of the monochromator/CCD camera. PL images were recorded as a function of rotation angle, with an exposure time of 30 ms. Figures 7.5 D and E are PL microscopy images of a single QB recorded with the polarizer at 180° (D) and 90° (E). Figure 7.5 F is a plot of the integrated PL intensity versus the polarization angle for the QB shown in E and F. The red line is a fit to a cos²θ dependence. The emission from a single QB is at a maximum when light is polarized parallel to the long axis of the QB, and is at a minimum when light is perpendicular to the long axis. This data is further evidence that QB structures are indeed 1-D systems. Unlike quantum dots and quantum rods, the anisotropic shape of 1-D structures can give rise to induced and/or permanent dipole moments. ³⁰ It has been previously reported that polarization anisotropies in quantum wires are due to the mixing of valence bands as a result from quantum confinement. ³¹-³³ In a study conducted by Lieber and co-workers, single InP quantum wires exhibited strong polarization anisotropies parallel to the wire axis. In addition to valence band mixing, the authors also attributed the polarization response to the large dielectric contrast between the wire and its surroundings. ³² Polarized emission has also been observed in single CdSe quantum wires. ³⁴-³⁸

Single CdSe QBs that did not exhibit strong blinking behavior when using a power density of approximately 100 W/cm² were used to study 1-D exciton delocalization. A small irradiation spot size with a diameter of approximately 425 nm was used to excite a spot in the middle of a long QB (l ≈ 1.2μm) (Figure 7.6). The
position of the irradiation spots are identified with a white circle on the PL microscopy images. A plot of the integrated intensity versus position of the PL microscopy image (Figure 7.6 A) illustrates that the PL from the QB is larger than the irradiation spot. The PL profile fits well to a Lorentzian shape, with a FWHM equal to approximately 1 micron. Since the PL from the QB is larger than the size of the illumination spot, the increase in breadth is attributed to exciton delocalization. Moving the illumination spot to the end of the QB (white circle in the microscopy image, Figure 7.6 B) decreases the overall integrated PL intensity measured from the QB. However, the maximum PL intensity remained in the center of the QB, and it did not shift towards the end of the QB near the illumination spot. If the emission were from only at the excitation spot, the maximum emission should have been from the excitation spot at the end of the QB. A fit to this PL image gives a sum of Lorentzians, and a FWHM equal to approximately 1.3 μm. This broadened PL shape is attributed to exciton delocalization. These experimental findings are further evidence that excitons in CdSe QBs behave as 1-D quantum mechanical particles.
Figure 7.6. PL microscopy images of a single QB, with the irradiation spot centered in the middle of the QB (A), and at the end of the QB (B). The white circles represent the illumination spot. The corresponding plots of the PL intensity profile versus position (black trace), with a Lorentzian fit (red trace), are plotted below each image. The dotted blue line shown in (B) represents a sum of Lorentzians.
7.4 Conclusion

In conclusion, CdSe QBs have shown to be promising contenders as 1-D systems due to their high PL QYs, ease of synthesis, polarized emission, and micron-length exciton delocalization. Their PL intensity is incredibly sensitive to air, but exposure to Argon gas decreases the effects of photobleaching. Single QBs exhibit emission polarized parallel to the long axis of the QB, and excitons can delocalize along the entire length of a QB, with distances up to 1.5 μm.
7.5 References


Chapter 8

Conclusions

The work in this dissertation has shown that one-dimensional excitons in single CdSe quantum wires are bound at room temperature. As discussed in Chapter 3, *Bound 1-D Excitons in Single CdSe Quantum Wires*, the emission behavior in single CdSe QWs is dictated by the local environment. In concentrated solutions, with excess synthetic reagents, the PL in single wires is exhibits emission steering. However, by diluting the sample, and thus reducing the density of synthetic reagents, the PL is not affected by the electric field. Therefore, bound excitons must be present. If individual electrons and holes were present, then they would localize towards their respective electrodes, and the PL would likely decrease. This was not observed. In chapter 4, *Bound Exciton Levels in One-dimensional Single Semiconductor Quantum Wires*, PL was observed from exciton levels within the first excited electronic state. A binding energy of 57 – 64 meV is reported using the hydrogen-atom model. Additionally, bound excitons were observed through exciton delocalization experiments, as described in Chapter 5, *Delocalization of 1-D Excitons Over Entire CdSe Quantum Wires*. In these experiments, the potential energy landscape of a single QW is modified by photo-filling trap sites with excess excitons photo-generated by using wide-field illumination. This modified potential can make conditions suitable for exciton delocalization along the length of the wire. Without photofilling the trap sites, excitons are likely to recombine non-radiatively, as evidenced by their low $\Phi_{QY}$, and do not delocalize along the length. Performing the experiments in
an external electric field verifies that bound excitons are responsible for delocalization, not individual charge carriers.

Exciton delocalization was also studied in 1-D CdSe quantum belts in Chapter 7, *Optical Properties and Spectroscopy of Single CdSe Quantum Belts*. Unlike Chapter 6, where two excitation sources were used to study delocalization in CdSe quantum wires, delocalization in the much shorter quantum belts (QBs) was studied using one excitation source, focused down to a diffraction-limited spot size ($\approx 425$ nm). When a single QB was excited in the center, the PL spanned almost the entire length of the QB (approximately 1.5 μm), well exceeding the diameter of the spot size. When the edge of the QB was excited, PL delocalized over the entire QB, and the intensity shifted towards the center of the belt.

Furthermore, in Chapter 6, *Low Temperature Spectroscopy of 1-D CdTe Quantum Wires*, I showed that the potential energy landscape of a wire is not uniform along the length, and that it can change with time. The potential energy landscape was investigated by cooling the wire down to cryogenic temperatures (4 K). At low temperatures, excitons can become stuck in potential energy minima along the length of the wire. The PL features become localized and discrete, representing emission from different energetic trap sites, and the band gap shifts to higher energy at low temperatures, as expected for semiconductors. Analyzing the spectra as a function of position indicates that the potential energy landscape is not uniform along the length. Additionally, comparing PL spectra at different times implied that the potential energy landscape can change with time or temperature.
In summary, I have shown that 1-D excitons in single CdSe QWs are bound, with a binding energy of approximately 57 – 64 meV, and that 1-D excitons can delocalize along the entire length of a wire, with distances up to 10 μm. Delocalization has also been observed in 1-D CdSe quantum belts. Additionally, I have shown that the potential energy landscape in a 1-D wire is not uniform along the length, and can change with time. This information is necessary to further the implementation of semiconductor quantum wires into optoelectronic devices or photovoltaic solar cells.
APPENDIX A

A.1  Exciton Density Estimates

The exciton density under cw excitation was estimated for the power densities used by considering the rate of exciton formation and the volume of the QW. These calculations were based on studies from Kuno and coworkers.\textsuperscript{1} The rate of exciton formation was calculated from the excitation power densities and the previously reported absorption cross section for CdSe QWs.\textsuperscript{2,3} We report numbers in units of excitons generated per area per time.

A.2  PL Peak Analysis

The contributions to the PL spectra from different emitting states were identified in two ways. Firstly, the second derivatives of the PL spectra were calculated, and the intensity maximum in each PL spectrum was set to the energy of the corresponding minimum in the second-derivative spectrum. Secondly, the PL spectra were fit to a sum of multiple Gaussians using a commercial least-squares fitting routine. After numerous iterations on numerous QWs it was found that spectra acquired using excitation densities of 0.80, 1.2, and 3.2 kW cm\textsuperscript{-2} fit well using two Gaussians. The four PL spectra recorded using the highest power densities fit well to the sum of three Gaussians (Figure 4.3).
A.3 PL Lifetime Measurements

The PL intensity decay profiles and lifetimes associated with the different emitting states in the CdSe QWs were extracted in a similar manner as described by Klimov et al. The decay profiles measured using the lowest excitation densities should represent the population decay of excitons in the $n = 1$ level with contributions from all non-radiative pathways and no spectral dependence. A commercial least-squares fitting routine was used to fit the PL intensity decay profile measured at the lowest excitation densities to a single-exponential decay. A mean value of the $n = 1$ level lifetime was obtained by measuring the lifetimes for numerous QWs. At slightly higher excitation densities the PL spectrum is believed to have spectrally overlapping contributions from both the $n = 1$ and perturbed $(n = 1)^*$ levels. In order to estimate the $(n = 1)^*$ level lifetime, the PL intensity decay profiles measured at a specific emission energy with the intermediate and lowest excitation densities were scaled so that the PL intensities at long times were the same. The difference between the two scaled decay profiles was taken to be the PL intensity decay associated with the perturbed $(n = 1)^*$ level. The resultant $(n = 1)^*$ decay profile was fit to a single-exponential decay, and measurements on numerous QWs were made to obtain a mean $(n = 1)^*$ lifetime. Since the PL spectra obtained using the highest excitation densities are believed to be dominated by emission from the $n = 2$ level, the decay profile associated with the $n = 2$ level was estimated by scaling and subtracting the profiles obtained at a lower emission energy with intermediate excitation density and at a higher emission energy with high excitation density. The resultant $n = 2$ PL intensity decay profile was fit to a single-exponential decay, and values from numerous QWs were used to obtain the mean $n = 2$ level lifetime.
A.4 PL spectra as a function of time

Figure A.1 Ten consecutively acquired PL spectra from the QW in Figure 4.1 excited with a power density of 126 W cm$^{-2}$ with a CCD integration time of 5 s (a) and 40 kW cm$^{-2}$ with a CCD integration time of 50 ms (b) per spectrum.
A.5 References