Optical Characterization of Charge Transfer Excitons in Transition Metal Dichalcogenide Heterostructures

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Abstract

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Two-dimensional materials such as graphene, boron nitride and transition metal dichalcogenides have attracted significant research interest due to their unique optoelectronic properties. Transition metal dichalcogenides (TMDCs) are a family of two-dimensional semiconductors which exhibit strong light-matter interaction and show great promise for applications ranging from more efficient LEDs to quantum computing. One of the most intriguing qualities of TMDCs is their ability to be stacked on top of one another to tailor devices with specific properties and exploit interlayer phenomena to develop new characteristics. One such interlayer interaction is the generation of charge transfer excitons which span the interface between two different TMDC monolayers.

This work aims to study the intrinsic optical properties of charge transfer excitons in TMDC heterostructures. We must first start by investigating methods to protect and isolate our sample of interest from its chemical and electrostatic environment. We demonstrate that near intrinsic photoluminescence (PL) linewidth and exciton emission homogeneity from monolayer TMDCs can be achieved using a combination of BN encapsulation and passivation of substrate hydroxyl groups. Next, we develop clean stacking techniques and incorporate low defect density source crystals to maintain intrinsic properties and ensure a sufficiently high quality heterostructure interface to study characteristics of charge transfer excitons in 2D TDMCs. Strong photoluminescence emission from charge transfer excitons is realized and is shown to
persist to room temperature. Charge transfer exciton lifetime is measured to be two orders of magnitude longer than previously reported. Using these high quality heterostructures, we study the behavior of charge transfer excitons under high excitation density. We observe the dissociation of charge transfer excitons into spatially separated electron-hole plasmas under optical excitation. We then probe properties of charge transfer exciton emission enhancement due resonant coupling to surface plasmon modes of gold nanorods.
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Dedication

To my Parents, Sister and Grandparents
CHAPTER 1

Introduction

Since the isolation of single-layer graphene in 2004, the field of two-dimensional materials has grown rapidly. Though graphene displays remarkable electronic and mechanical properties, it is severely limited by the lack of an electronic bandgap. The wealth of possible applications for two-dimensional semiconducting materials in optoelectronics includes use as photodetectors, diodes and transistors. This prompted the expansion into unexplored materials such as transition metal dichalcogenides (TMDCs).

TMDCs are a class of materials of the form MX$_2$ where M is a transition metal atom, (highlighted in columns 4-10 in Figure 1.1), and X is a chalcogen atom, (highlighted in orange in Figure 1.1). In the monolayer limit, these materials have direct bandgaps in the visible and near infrared regions. Quantum confinement from the two-dimensional nature of these monolayers results in large exciton binding energies, allowing them to be stable at room temperature.$^1$ These properties make them ideal candidates for applications in commercial light sources and detectors. Additionally, The monolayers of TMDCs lack inversion symmetry, which allows the K and K' valleys in momentum space to be distinguishable. Band splitting due to spin-orbital coupling results in a spin-dependant bandgap. The fields of spin- and valley-tronics have been created on the principle of using these newly discovered spin and valley degrees of freedom for use in quantum computing$^{2-4}$. Combining different two-dimensional materials which exhibit these phenomena in the same structure allows for further exploration of device possibilities by tailoring devices with desired specific properties and exploiting interlayer interactions.
This work has two major goals. The first goal is to develop clean stacking technique with low defect density materials to maintain intrinsic properties and ensure a sufficiently high quality heterostructure interface to study characteristics of charge transfer excitons in 2D TDMCs. To achieve this goal, we must not only perform a clean heterostructure fabrication procedure, but also precisely align the crystallographic lattices of the constituent monolayers to ensure efficient charge transfer. The second goal is to study intrinsic properties of charge transfer excitons. Specifically, we investigate the dissociation of charge transfer excitons into spatially separated electron-hole plasmas at high excitation density and properties of emission enhancement due to coupling to resonant gold nanorod surface plasmons.

Figure 1.1: (Above) Periodic table indicating chalcogen elements (orange) and transition metal elements (all other colors).

Figure 1.2: (Below) Diagram of crystal structure of layered TMDC material.
1.1 Background

1.1.1 Crystal Structure of Transition Metal Dichalcogenides

Solids of TMDCs form in layers, which are strongly bound together in plane but weakly bound out of plane by van der Waals forces. The bonding structure allows these materials to be exfoliated down to a single monolayer with a thickness of one unit cell. A hexagonal close-packed primitive cell is shown in Figure 3, where the M atoms are shown in blue and X atoms in green. When observed from above, the lattice appears as a honeycomb pattern, comprised of a series of hexagons. The crystallographic orientation of this type of lattice structure is defined by the directions of the armchair and zigzag edges.

1.1.2 Electronic Band Structure in 2D

Electronic band structure arises from the wavefunction overlap between neighboring atoms. The overlap of electron clouds in a periodic structure forms an electrostatic potential environment which follows the periodicity of the crystal lattice. The electrons in the crystal
lattice are described by general Bloch functions, which are wavefunctions that satisfy Schrödinger's equation in a periodic potential. The solutions are of the form:

$$\psi_k(x) = e^{ikx}u_k(x) \quad \text{where} \quad u_k(x + a) = u_k(x)$$  \hspace{1cm} [1]

To determine the specific functional form of $u_k(x)$, the Kronig-Penney model is applied. This model specifies the periodic potential in Schrödinger's equation as a series of square well functions. To solve for allowed energies, the boundary conditions applied are the continuity and the periodicity of both the wavefunction and its derivative. Only select energy regions satisfy these boundary conditions, which are called bands. These bands of allowed states are separated by forbidden states called energy bandgaps.

Though there are multiple regions of allowed and forbidden energy bands, we focus on the forbidden gap which encompasses the material Fermi energy, and the allowed energy bands directly surrounding it. The Fermi energy is the energy below which all allowed electronic states are filled and above which all allowed electronic states are unoccupied, assuming no thermal excitation. As the electrostatic potential varies spatially over the unit cell, the allowed energy bands also vary. There are resultant peaks and valleys of energy bands at different positions in real and momentum space, which will be further explored in the following paragraph. If the minimum energy distance between a higher energy band valley and lower energy band trough is located at the same crystal momentum, the bandgap is called direct. Otherwise, it is known as indirect. For the materials of interest in this work, MoSe$_2$ and WSe$_2$, in the monolayer limit there exists a direct bandgap at the K points of the first Brillouin zone, as shown in Figure 1.
The Brillouin zone is the Fourier Transform of the periodic direct (real space) crystal lattice unit cell into momentum space. A wavefunction defined by a position in real space can be represented by its Fourier transform in a point in momentum space. Solutions to Schrödinger's equation in a periodic lattice can be completely characterized in the first Brillouin zone in reciprocal space. Therefore, the first Brillouin zone contains all the wave vectors which are allowed in the real space crystal lattice. For a hexagonal unit cell in real space (Figure 1.6a), the first Brillouin zone is also hexagonal in momentum space, (Figure 1.6b). Also shown in Figure 1.6b are the high-symmetry critical points Γ, K and M in the first Brillouin zone of a hexagonal lattice. Because the direct bandgaps of both MoSe$_2$ and WSe$_2$ are located at the same position in momentum space (K points), they are also located at the same position in each unit cell in the real space lattice.

Figure 1.5: K-space energy band diagram for monolayer MoSe$_2$ (a) and WSe$_2$ (b).

Figure 1.6: Real space lattice (a) and first Brillouin zone (b) of a hexagonal crystal lattice.
1.1.3 Excitons

Excitons are quasiparticles comprised of an electrostatically bound electron and hole pair. They can be formed when TMDCs absorb a photon of energy greater than or equal to their bandgap. The energy absorbed is transferred as a driven coherent oscillation of the electron cloud by the photonic oscillating electromagnetic field.

Because of their two-dimensional nature, excitons in TMDC monolayers experience reduced dielectric screening. Just as with any pair of oppositely charged particles, an electric field is produced between the electron and the hole which comprise an exciton. The resulting Coulomb force defines the strength with which they are bound. In three dimensions, the electron clouds of atoms within the region of this field will shift such that they counter the field. As a result, the binding energy of the exciton is reduced. Diffuse excitons and those in high dielectric constant materials may have their binding energy reduced to zero, at which point they become free carriers. In 2D materials, the generated electric field only encompasses a small volume inside the monolayer itself. Out-of-plane, little to no Coulomb screening is provided, assuming the monolayer is in a low dielectric environment such as air. As a result, excitons in 2D materials often exhibit large exciton binding energies, allowing them to remain stable even at room temperature.¹

![Figure 1.7: Electric field lines between an electron-hole pair in three (a) and two (b) dimensional crystals.](image)

¹ Reference: [1]
Exciton recombination at the bandgap of a semiconductor can result in the emission of a photon. Excited electrons undergo non-radiative relaxation from their initial above-gap excited state to a bandgap minimum with the assistance of lattice phonons. The minimum energy in the conduction band is modified by the exciton binding energy such that the energy of the emitted photon is:

\[ E = E_G - E_B \]  

where \( E_G \) is the original bandgap energy and \( E_B \) is the exciton binding energy. From this description, a delta function emission distribution is assumed at the central emission frequency with energy exactly equal to the known transition energy in equation [2].

\[ I(\omega) = \delta(\omega - \omega_0) \text{ where } \omega_0 = \frac{\hbar}{E} = \frac{\hbar}{E_G - E_B} \]  

However, natural spectral broadening occurs due to the limitations imposed by Heisenberg’s Uncertainty Principle:

\[ \Delta E \Delta t \geq \hbar \]  

where \( \Delta E \) is the width of the emission spectrum at half maximum (FWHM) and \( \Delta t \) is the lifetime of the excited state. The intrinsic spread in emitted photon energies is the minimum of this inequality. Using equation [4] and \( E = \hbar \omega \), provides the following equations:

\[ \Delta E = \frac{\hbar}{\Delta t} \text{ and } \Delta \omega = \frac{\Delta E}{\hbar} = \frac{1}{\Delta t} \]  

Therefore, the emission spectrum and excited state lifetime are fundamentally linked and limited by the other.

The transition of the system from an excited state to a ground state, including the spontaneous emission of a photon occurs over a characteristic lifetime which inherently broadens the emission spectrum, as discussed in the previous section. A Lorentzian emission lineshape can
be derived by modeling the system as a damped harmonic oscillator, as was done by Demtroder et al. The oscillation amplitude follows the damped harmonic oscillator equation of motion:

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = 0$$  \[6\]

where the damping coefficient, $\gamma$, is the result of radiative energy loss and $\omega_0$ is the central emission frequency in the undamped case. As the variable $t$ denotes time after excitation, we take $x(t < 0) = 0$. Using the boundary conditions $x(0) = x_0$ and $\dot{x}(0) = 0$, we describe the oscillation amplitude by:

$$x(t) = x_0 e^{-\gamma t/2} \left[ \cos(\omega t) + \frac{\gamma}{2\omega} \sin(\omega t) \right]$$  \[7\]

Assuming a very small damping ($\gamma \ll \omega$), the second sinusoidal term can be neglected and the oscillation amplitude is now described by:

$$x(t) = x_0 e^{-\gamma t/2} \cos(\omega t)$$  \[8\]

and is plotted as a solid line in Figure 1.8(a). The dashed line in this figure denotes the envelope which outlines the oscillation damping with time. By taking the Fourier Transform of equation 
, we define an oscillation amplitude in the frequency domain:

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} x(t) e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int_{0}^{\infty} x_0 e^{-\gamma t/2} \cos(\omega t) e^{-i\omega t} dt$$

$$A(\omega) = \frac{x_0}{\sqrt{8\pi}} \left[ \frac{1}{i(\omega-\omega_0)+\gamma/2} + \frac{1}{i(\omega+\omega_0)+\gamma/2} \right]$$  \[8\]

We take $(\omega - \omega_0) \ll (\omega + \omega_0)$ and therefore neglect the second term in which $(\omega + \omega_0)$ appears in the denominator. The intensity of the emission spectra is then found by:

$$I(\omega) = A(\omega) A^*(\omega) = \frac{x_0^2}{8\pi} \left( \frac{1}{(\omega-\omega_0)^2 + (\gamma/2)^2} \right)$$  \[9\]

Normalizing this function to a maximum intensity of 1, we reach the emission intensity as a function of frequency:
which is a Lorentzian function with a FWHM of $\Delta \omega = \gamma$, as shown in Figure 1(b). We can see from this and equations that

$$\Delta \omega = \frac{\Delta E}{\hbar} = \frac{1}{\Delta t} = \gamma = FWHM$$

Therefore, the lifetime of the excited state in the transition, $\Delta t$, describes the fundamental lower limit to the emission linewidth

\[ I(\omega) = \left( \frac{\gamma/2\pi}{(\omega-\omega_0)^2 + (\gamma/2)^2} \right) \]  

1.1.4 Defects

Lattice defects are any disruption in the periodic repetition of the unit cell pattern which comprises the crystal structure. Point defects, in which atoms are missing from the lattice or replaced by different elements, are the most common type of lattice defects found in TMDC monolayers. The resulting local distortion of the crystal lattice affects the wavefunction overlap between atoms in the lattice and thus also affects the local electrostatic environment and band structure. These defects have been shown to cause decreases in electron mobility in graphene as well as quenched photoluminescence in other two-dimensional materials. In semiconductors, defects have been shown to create scattering centers, localized sub-bandgap trap states, and non-
radiative recombination centers which can cause non-radiative pathways to outcompete radiative recombination pathways.\textsuperscript{15-18} The effect can be seen as sub-bandgap emission, quenched photoluminescence at the exciton resonance, and short excitonic lifetime. Further consequences of defect-laden material will be discussed in Chapter 3.\textsuperscript{19}

1.1.5 Heterostructures

Heterostructures are engineered devices in which several monolayers of different two-dimensional materials are layered on one another. By stacking TMDCs, we can engineer devices with specific optical and electric properties and develop materials with novel characteristics due to interactions between layers.\textsuperscript{9, 10, 20-22} The MoSe\textsubscript{2}-WSe\textsubscript{2} heterostructures on which this work focuses exhibits type II band alignment, meaning both feature a direct bandgap, but display an offset in conduction and valence band energies.

![Diagram of type-II band alignment.](image)

The resulting conduction band minimum resides in the MoSe\textsubscript{2} layer and the valence band maximum resides in the WSe\textsubscript{2} layer, as seen in Figure 1.9. A new energy difference minimum is formed between the WSe\textsubscript{2} valence band and the MoSe\textsubscript{2} conduction band, called a pseudo-gap; the pseudo-gap is labeled as $\Delta E$ in Figure 1.9. As a consequence, excitons excited in either layer can spontaneously diffuse, such that electrons reside in the MoSe\textsubscript{2} layer and holes reside in the
WSe₂ layer. Figure 1.10 depicts the charge transfer process in a TMDC heterostructure with type II band alignment.\textsuperscript{23}

In TMDC heterostructures, electrons and holes that are bound across the material interface form quasiparticles known as interlayer or charge transfer (CT) excitons.\textsuperscript{8-10, 20-22, 24} Due to the large spatial separation of CT excitons, they are predicted to have extremely long lifetimes of hundreds of nanoseconds or microseconds.\textsuperscript{8} The long lifetime and the physical separation of carriers are advantageous for photovoltaic applications.\textsuperscript{8, 21, 24} In addition, electrons and holes organized in separate layers form a vertical p-n junction, giving TMDC heterostructures the potential to be used in novel nanoscale optoelectronic devices, such as photodetectors and photodiodes.\textsuperscript{8, 21, 24}

![Figure 1.10: (a) Diagram of charge transfer in heterostructures with type-II band alignment. (b) Schematic depicting charge transfer excitons bound across the heterostructure interface.\textsuperscript{23}](image)

The fabrication of heterostructures for most efficient CT exciton formation requires crystallographic alignment. In Figure 1.11, the hexagonal first Brillouin zone for each of the constituent monolayers is shown overlapped and positioned with a relative twist angle of Δφ. A nonzero Δφ causes a momentum offset between the K-points of the MoSe₂ and WSe₂ layers, denoted as k_{CT} in Figure 1.11, which must be overcome for charge carrier diffusion and subsequent CT exciton formation to occur. To efficiently allow for radiative recombination of
these excitons, the momentum offset between the conduction band minimum in MoSe₂ and valence band maximum in WSe₂, denoted as k_{CR}, must be minimized to eliminate the need for phonon assistance in the recombination process^{10, 11, 21}. Minimization can be accomplished by aligning the crystal lattices of these materials, thereby minimizing twist angle Δφ and momentum space offset between the Brillouin zone K-points^{9-11, 21}.

![Diagram of the hexagonal first Brillouin zones rotated with respect to one another by an angle Δφ.](image)

In 2015, Yu et al proposed that the imperfect twist angle between layers and the resulting lattice mismatch in 2D TMDC heterostructures could lead to six-fold symmetric light cones with finite velocities in the energy dispersion of the interlayer exciton. They defined these light cones as areas of exciton phase space in which phonon assistance is not required for exciton recombination. To conserve momentum in the case of a small lattice mismatch, the total momentum of the electron and the hole must equal the momentum offset between the K-valleys in the opposite layers. They showed this condition can only be met with rotational lattice mismatch in multiples of 60° and that efficient charge transfer can only take place within about ±5° from this perfect alignment^{10}.

Though a comprehensive study on relative crystal orientation in heterostructures is still lacking, it has been well-established that in structures of two monolayers of the same material
(homobilayers) relative crystal orientation has a major effect on interlayer coupling strength, and therefore on charge transfer. In MoS$_2$ homobilayer systems, the variation of interlayer spacing with lattice twist angle has been established as the source of this effect. Interlayer separation in MoS$_2$ homobilayers is mainly due to repulsion between sulfur atoms in the two monolayers. At twist angles of 0° and 60°, Density Functional Theory (DFT) calculations show that the most energetically favorable lattice configuration occurs when the sulfur atoms of one layer are placed over the interstitial space between the sulfur atoms of the other layer. This lattice configuration minimizes the interaction between adjacent sulfur atoms, which in turn minimizes interlayer spacing. A diagram of interlayer spacing for different stacking configurations can be seen in Figure 1.12. We can see that interlayer spacing minima occur for when sulfur atoms are stacked on molybdenum atoms or at interstitial sites. At any other twist angle, interaction, and therefore repulsion, between sulfur atoms is greater, which increases interlayer spacing.

![Figure 1.12: Interlayer spacing for different lattice rotational orientations in hexagonal lattice bilayers](image)

DFT with a local density approximation has been used to compute the electronic band structure of MoSe$_2$-WSe$_2$ heterostructures by several groups$^8$, $^{26}$, $^{27}$. All agree that interlayer electronic band hybridization is negligible at the K-points in the first Brillouin zone. As a result, the electronic band structure is a superposition of the constituent monolayer electronic structure at that momentum. Latini et al. modeled heterostructures the band structure of heterostructures of
two twist angles, 16° and 34°, and found no significant difference in the electronic band structure between them. From Figure 1.12, we can see the interlayer coupling should be comparable at 16° and 34° since the interlayer spacing is roughly constant at these twist angle values. Though far from the lattice alignment position, Latini et al. chose two twist angles of 16° and 34° to minimize strain in the commensurate heterostructure lattice.

My work centers around heterostructures composed of MoSe₂ and WSe₂ monolayers. These particular TMDCs both have hexagonal crystal structure and lattice constants which differ by only 0.1%. Once crystallographically aligned, these two materials are well suited to be very close to a natural bilayer, minimizing interlayer spacing and induced strain as well as maximizing the area over which the lattices are commensurate.

Lattice alignment is a necessary feature for efficient CT exciton emission, but cannot compensate for defect-mediated non-radiative recombination pathways. Zhu et al. fabricated various MoS₂-WS₂ heterostructures with different relative orientations. They attempted to study the change of CT exciton dynamics with twist angle in TMDC heterostructures. Even with precisely fabricated heterostructures with twist angle close to 0°, no CT exciton PL emission was observed. Transient reflectance showed a charge transfer time of less than 40 fs. This upper limit on charge transfer time was found to be independent of twist angle. Time-resolved PL measurements on the different samples showed exciton lifetimes ranging from a few picoseconds to a few nanoseconds with no clear correlation to twist angle. The researchers carried out excitation density and gate-dependent experiments, which ruled out Auger recombination as a dominant exciton recombination mechanism. Therefore, they concluded that recombination was largely defect-mediated. This work demonstrates the importance of using high-quality, defect-
free materials to successfully enable charge transfer and radiative recombination in TMDC heterostructures.

1.1.6 Plasmonic Structures and Emission Enhancement

A surface plasmon is a coherent oscillation of conduction electrons in a metal, localized to the interface between a metal and dielectric. Surface plasmons can be excited by interaction with an oscillating resonant electric field such as that of an incident photon. The resulting electron cloud displacement from positively charged nucleus creates a resonantly oscillating electric field which extends as an evanescent field beyond the boundaries of the metal itself. This enhancement of the local electric field in near-field of nanoparticles creates an enhanced local density of states. Fermi’s Golden Rule defines the probability of an electronic transition with the presence of a perturbing electromagnetic field as:

\[ P_{\text{ef}} = \frac{2\pi}{\hbar} |< \psi_f | H' | \psi_i >|^2 \rho(E_f) \]  \[ \text{[12]} \]

where \( H' \) is the applied perturbation, \( \rho(E_f) \) is the density of final energy states, and \( \psi_{f,i} \) are the final and initial states, respectively. By enhancing the local density of states, the probability of this transition increases, as does the transition rate. This phenomenon is known as the Purcell effect\(^3^0\).

Many studies have been done exploiting this uniquely nanoscale phenomenon to enhance emission from fluorescent molecules, quantum wells, and LEDs\(^3^1\)-\(^3^3\). Most have pumped both the emissive material and the nanoparticles or plasmonic structures resonantly. In this case, not only is the Purcell effect increasing the rate of photon emission, but the surface plasmon energy can be resonantly transferred to generate additional excitons in the emissive material. Additionally, the excited surface plasmons lack the momentum matching condition for photon emission
imposed on the exciton. As a result, a type of feedback loop can occur in which the applied plasmonic structures create an additional radiative emission pathway\textsuperscript{32-37}.

\textbf{1.2 Overview of this Work}

In this thesis, I will address specific issues pertaining to heterostructure fabrication and charge transfer exciton characterization and emission modulation. First, I will investigate the intrinsic optical characteristics of monolayer MoSe\textsubscript{2} using low temperature photoluminescence spectroscopy. I will present an analysis of BN encapsulated monolayer properties which will demonstrate the clean material and transfer process necessary for charge transfer in TMDC heterostructures. Next, I will discuss fabrication techniques for aligned MoSe\textsubscript{2}-WSe\textsubscript{2} heterostructures. Characterization of the charge transfer exciton will be provided through analysis of photoluminescence and time-correlated single photon counting measurements. I will then discuss characteristics of electron-hole plasma formation in TMDC monolayers under high fluence excitation. Specifically, I will present experiments in which interaction between excitons in a high density environment will lead to dissociation of the carriers, forming a free electron plasma in one layer and free hole plasma in the other. Finally, I will discuss the enhancement of charge transfer PL emission by coupling to resonant surface plasmons in gold nanorods. I will conclude with a discussion of continuing efforts to produce pristine heterojunction interfaces as well as the need for further study of the coupling mechanism between charge transfer excitons and plasmonic structures.
CHAPTER 2

Experimental Techniques

2.1 Device Fabrication

We perform mechanical exfoliation of bulk grown single crystals in order to isolate monolayers or flakes of desired thickness for each material. To start this process, a piece of Scotch tape is fixed to a flat surface at each end with the adhesive side exposed. A small amount of bulk crystal is spread over an area of the tape about 1” long. The tape is folded over, creasing at the point where the bulk material ends such that the portion of tape with material lays on a portion of the tape without material. This process is repeated, taking care to not overlap bulk crystal on bulk crystal, until the whole tape is covered. Avoiding overlap of bulk crystal helps minimize breakage of single crystals, allowing for larger monolayers. This first tape is generally has too thick of a bulk crystal layer on it to be used in exfoliation directly, and is instead used as a master. A daughter tape is made from the master tape by forcefully pressing onto it a second tape of the same length and peeling them apart. The daughter tape will have a significantly thinner layer of bulk crystal adhered to it and will be used for exfoliation. Each master tape can generally produce three daughter tapes, depending on the thickness of the initial bulk crystal applied to it. All tapes are stored in an inert nitrogen gas environment to avoid degradation.

The substrate used in exfoliation is a silicon wafer with 285 nm SiO$_2$ thin film surface. The wafer is diced into $1\text{cm}^2$ chips and cleaned by oxygen plasma etching for 30 seconds. To exfoliate material, the daughter tape is pressed forcefully onto a chip. With the tape adhered to the chip, both are heated at 90° C for about 2 minutes. Once removed from the heat, the chips
and tape are left to cool passively. The tape is quickly peeled off the chip surface and crystal flakes of varying thickness are left on the chip surface. The chips are observed under an optical microscope and potential monolayers of the TMDCs are identified by optical contrast. The single-layer nature is confirmed through atomic force microscopy (AFM) and Raman spectroscopy.

A dry-stacking technique is used to maintain pristine interfaces between layers. Commercially grown MoSe$_2$ single crystals are mechanically exfoliated by the standard Scotch-tape method with the addition of heating the substrate to 90°C while it is in contact with the bulk crystal and tape. This process is repeated for BN crystals, without heating. Atomic force microscopy is carried out on BN flakes to ensure an atomically smooth surface and to verify flake thickness.

A Polydimethylsiloxane/Propylene Carbonate (PDMS/PC) microlens is used to assemble the stack. A drop of PDMS is placed on a plain glass slide and allowed to cure in a semispherical shape. Once cured, a thin film of PC is fabricated by compressing a 6 wt% PC/chloroform solution between two microscope slides and shearing the slides apart. The result is a thin layer of the PC solution on each slide which becomes a solid film once the chloroform evaporates. The film is carefully lifted off the slide and placed over the PDMS microlens; care is taken to avoid creating wrinkles or bubbles in the film. The slide, microlens and film are then heated to 180°C to cure the PC film. Using the microlens, the components of the stack are picked up sequentially starting with the top BN, TMDC monolayer and finishing with the bottom BN. A schematic of the transfer stage and PDMS microlens is shown in Figure 2.1. Between each subsequent flake pickup, the slide is heated to 90°C for about 10 minutes to smooth out roughness in the PC film which may have arisen in the previous pickup procedure.
The microlens slide is secured polymer-side down in the transfer arm of our in-house-built transfer stage. The exfoliated chip is secured under the slide on a heater-enabled stage by a vacuum chuck. The flake of interest is located using a 2x microscope objective and looking through the slide and polymer to the SiO₂ surface. For the first pickup, the slide is positioned such that the target flake will be in contact with the polymer just off the inflection point of the curved microlens. The inflection point concentrates stresses during the pickup process and flakes adhered there have a higher chance of cracking during pickup. Once positioned, the microlens is lowered until just before contact with the flake and substrate. The stage is then heated to 80° C, causing the PC film to expand as it heats and to make contact with the substrate surface. The contact area will expand over the flake of interest. After being held at high temperature for 5-10 minutes, the stage is allowed to cool passively to 50° C. Once cooled, the microlens is slowly raised off of the substrate, picking up the flake of interest. This process is repeated for all constituent layers of the sample being fabricated with the modification of using a 20x objective in order to align the subsequent flake with the previous flake. Once all layers are picked up onto the microlens, the entire sample can be transferred onto a substrate of choice. To transfer the sample, the sample and microlens are put in contact using the same method as the pickup procedure. The stage temperature is then raised to 190° C in order to melt the PC film onto the substrate. The PC residue is then cleaned by soaking the chip with the sample in chloroform.

![Figure 2.1: Schematic of transfer stage, slide with PDMS/PC microlens.](image-url)
2.2 Photoluminescence

Photoluminescence (PL) spectroscopy is an optical technique used to probe electronic band structure in a material. A high energy laser is used to excite the material, causing available high energy electronic states to become populated. In a semiconducting material, photon energy greater than the bandgap energy is used, resulting in high energy electrons populating the conduction band of the material and creating holes in unoccupied states of the valence band. Low to moderate excitation intensity creates bound excitons while high excitation intensity can generate free electron plasma in the material. PL studies of the former will be discussed in Chapters 3, 4 and 6 while the latter will be detailed in Chapter 5. These excited electrons relax non-radiatively to the band edge at which point they recombine with the holes and each emit a photon of energy equal to the bandgap energy. Phonon interaction expands the momentum space in which optical transitions can take place, increasing the range of photon energies and broadening the measured PL peak. To reduce this effect, all measurements are conducted at cryogenic temperatures unless otherwise noted. A diagram of the experimental setup is provided in Figure 2.2. For our measurement, we use a continuous wave (CW) 532nm diode laser as an optical pump. The beam is focused through a 100x objective onto the sample surface. PL emission and the reflected beam pass through the same objective before being sent either to a CCD camera or through a 600 nm high-pass filter to a spectrometer.

![Diagram of photoluminescence spectroscopy setup.](image)

*Figure 2.2: Diagram of photoluminescence spectroscopy setup.*
2.3 Time-Correlated Single Photon Counting

Time-correlated single photon counting (TCSPC) is a transient spectroscopic technique used to determine decay rate and lifetime of photoinduced excitons. For this measurement, we use a similar experimental setup as for static PL previously mentioned. However, instead of 532 nm CW light, we use a 680 nm 150 fs pulsed laser source with a time resolution of 40 ps. Low power excitation (hundreds of nanowatts) is used to generate a small number of excitons in the material. A schematic of our experimental setup is provided in Figure 2.2. The pump pulse triggers a timer to start. As the excitons decay, the emitted photons are detected by a silicon avalanche photo diode (APD) which is able to detect single photons. The first incident photon triggers the timer to stop. Since the photon is emitted as an induced exciton recombines, the time recorded is the lifetime of one exciton. This process is repeated for thousands of pulses, recording an exciton lifetime for each instance. The result is a histogram showing the frequency of photon emission at a given time after excitation. The TCSPC data is fit using a decaying exponential. The inverse of the decay rate fit parameter will yield the characteristic exciton lifetime in the material.

![Diagram of time-correlated single photon counting setup.](image)

**Figure 2.3:** Diagram of time-correlated single photon counting setup.
2.4 Transient Reflectance

Transient reflectance is a pump-probe measurement used to determine how electronic state occupation varies with time. For this measurement, samples are first optically pumped into an excited state. Over time, excited electrons relax back down to the ground state. After a time delay, a probe pulse is incident on the sample. If higher energy states are still occupied, electrons still in the ground state will not be able to be excited into higher energy states resonant with the probe energy. Therefore, the probe pulse absorption will be decreased with respect to ground state incidence and more of the probe beam will be reflected. Reflectance contrast is defined as the difference in reflectance of the sample in the ground state versus excited state after delay time Δt, normalized by the sample reflectance in the ground state:

\[
\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0}
\]

[13]

where R is the reflectance of the excited sample after a delay time Δt and \( R_0 \) is the reflectance of the ground state sample.

In our experiments, samples are pumped using a 1.83eV, 150 fs pulse and probed with broadband white light of 1.2-1.8 eV. Using this measurement, we can determine induced absorption and photo-bleaching in the sample at different energies and times after pumping. Photo-bleaching occurs due to depletion of ground state carriers from excitation to a higher energy state. While the carriers remain in their excited state, any incident photon of appropriate energy to induce a transition has a low probability of absorption and is instead reflected. Therefore, the reflectance of a sample gives a measure of the number of carriers remaining in their excited state a given time after the pump pulse is incident. Induced absorption is the additional absorption of a photon by an electron already in an excited state.
By using a broadband white light probe, we can determine which of a range of transitions are available to ground state excitation, photo-bleaching or induced absorption. Discerning these mechanisms from the transient reflectance spectrum allows us to determine the landscape of exciton states at a given point in time\textsuperscript{38,39}.

2.5 Second Harmonic Generation Spectroscopy

Second harmonic generation is a nonlinear optical phenomenon in which a coherent optical pump results in a generated coherent optical output. The principle behind second harmonic generation can be explained using an anharmonic oscillator model. The electronic field of the incident light drives oscillation of the electron cloud about the fixed nuclei of atoms in the lattice, resulting in an induced polarization of the material. The displacement of the electrons with respect to an applied electric field amplitude is linear for small amplitudes, but becomes nonlinear for more intense incident light. The effect of this nonlinear relationship is described by the nonlinear optical susceptibility tensors, $\chi^{(n)}$, $n>1$. Susceptibilities are related to material properties and crystal symmetry. The ensemble average of the polarization of the material due to an applied electric field, $E(k,\omega)$ is given by

$$< P(\omega) > = < P^{(1)}(\omega) > + < P^{(2)}(2\omega) > + < P^{(3)}(3\omega) > + \cdots $$ \[14\]

where the order of each term indicates the harmonic emission due to nonlinear absorption of incident photons\textsuperscript{40}. Third order and higher susceptibilities are generally very small and generally require vastly more laser power to induce a 3rd harmonic signal. The term $P^{(2)}$ describes polarization which contributes to second harmonic generation in the material and is related to the electric field component of the incident light by:
\[ P^{(2)}(2\omega) = \varepsilon_0 \chi^{(2)}(2\omega):E(\omega)E(\omega) \]  

where \( \varepsilon_0 \) is the material dielectric function and \( \chi^{(2)} \) is the material second order nonlinear electric susceptibility tensor. TMDC monolayers are single crystals of symmetry group D_{3h} and therefore have nonzero components of \( \chi^{(2)} \): \[
\chi^{(2)}_{yyy} = -\chi^{(2)}_{yxx} = -\chi^{(2)}_{xx} = -\chi^{(2)}_{xyx}
\]

We can see from the double dot product in equation [15], the nonzero tensor components modify the direction of polarization of the resulting second harmonic emission.\(^{41}\)

In the fabrication of crystallographically aligned devices, second harmonic generation spectroscopy is used to determine the armchair direction orientation of the TMDC crystal lattice in constituent monolayers. Linearly polarized 800 nm, 100 fs pulsed laser light is focused using a 100x objective to pump the monolayer. The 400 nm second harmonic signal is collected through the same objective and filtered through a short-pass dichroic mirror, short pass and band pass filters to ensure elimination of the fundamental wavelength. A linear polarizer is placed in the collection path to only collect emitted light either co-polarized or cross-polarized with respect to the incident light - the total second harmonic emitted light intensity remains constant with different orientations. However, the intensity of the emission of the co- and cross-polarized emission is dependent on the lattice orientation of the monolayer relative to the orientation of the polarization of the incident laser light.

Emission intensity from each monolayer sample is measured for different orientations by rotating either the sample or the incident polarization and detecting a fixed polarization. It is well
established that the intensity of the SHG emission from the TMDC monolayer varies with the relative angle from the excitation beam polarization as

\[ I_\perp(2\omega) \propto \cos^2 (3\theta) \]  \hspace{1cm} [17]

\[ I_\parallel(2\omega) \propto \sin^2 (3\theta) \]  \hspace{1cm} [18]

where \( \theta \) is the angle between the incident laser polarization and the armchair lattice direction\textsuperscript{41-43}. Subscripts \( \parallel \) and \( \perp \) indicate co- and cross-polarized SHG emission intensity with respect to the polarization of the pump laser. The incident laser light polarization is known. Fitting the measured data to this function determines a value for \( \theta \). A representative data sample from measuring cross-polarized emission and fit by equation [17] can be seen in Figure 2.3. From this, we determine the lattice orientation of the TMDC monolayer in the frame of the SHG measurement setup.

Figure 2.4: Second harmonic generation spectroscopy data and fit.
The fabrication and measurement techniques discussed in this chapter will form the basis of the experiments in the following chapters. All of the samples used in these experiments are fabricated using the clean stacking techniques outlined in this chapter. Second harmonic generation spectroscopy is employed to determine lattice orientation for aligned heterostructure fabrication in Chapters 4-6. Photoluminescence measurements will serve as a baseline metric indicating relative favorability of radiative recombination pathways to non-radiative recombination pathways for both intra- and interlayer excitons for all following experiments. Exciton lifetimes extracted from TCSPC data along with the functional form of the TCSPC data itself will serve as a comparison against theory as a metric of sample quality in Chapters 3 and 4. In Chapter 5, TCSPC and transient reflectance are used to confirm the presence of an electron-hole plasma in our heterostructure.
CHAPTER 3

Intrinsic Limitations of MoSe$_2$

Photoluminescence Linewidth

3.1 Introduction

The ultimate goal of this work is to study the intrinsic optical properties of charge transfer excitons in TMDC heterostructures. However, lattice alignment and mediation of lattice defects are not the only obstacles to accomplishing this task. We have seen from previous studies discussed in Chapter 1 that environmentally induced disorder creates non-radiative pathways which dominate charge transfer exciton recombination. The local electrostatic, mechanical, and chemical environment of a sample introduces disorder in the form of recombination centers, electrostatic doping and strain, which warp band structure and can provide significant non-radiative decay channels$^{19}$. The consequence of this is the obstruction of intrinsic properties. It is clear that a comprehensive study of charge transfer in TMDC heterostructures cannot be realized until we can confidently fabricate heterostructures which preserve a material's intrinsic optoelectronic properties.

In this chapter, we discuss methods to protect and isolate single monolayer TMDCs from their electrostatic and chemical environment. Boron nitride encapsulation is introduced to prevent adsorption of atmospheric molecules and create distance between the monolayer and the substrate electrostatic environment. Substrates are also treated with a self-assembling monolayer (SAM) which neutralizes dangling bonds on the SiO$_2$ surface. We use PL intensity and linewidth as metrics for induced disorder in our samples. The relative intensity of PL emission of the trion and exciton states is also discussed as a measure of electrostatic charge neutrality of the sample.
3.1.1 Crystal Source

The crystal quality of commercially grown TMDC bulk single crystals lags far behind that of more traditional semiconductors such as silicon or gallium arsenide. Chemical vapor transport (CVT) most commonly used growth technique in industry because it is faster and safer than other methods since it requires lower growth temperatures. The flux growth method is a relatively new growth technique shown to produce higher quality bulk single crystals. CVT and flux growth methods use similar fundamental method: component materials (Mo, W, S, Se) and a transport material are sealed at a far end inside a quartz ampoule on one side of a section of quartz wool. This end of the ampoule is heated at the end holding the raw material, creating a temperature differential along the length of the ampoule. As the ampoule is cooled, TMDC crystals begin to form in the cooler, end. The main difference between these two methods is that in CVT, the transport agent is usually a halogen such as iodine. The flux method instead uses the constituent chalcogen as a transport agent. The flux-grown resultant crystals have been shown to have 2 orders of magnitude lower defect density as compared to commercially grown CVT crystals. The optical properties of monolayers exfoliated from flux grown crystals are greatly improved as a result. The FWHM of the exciton PL emission halved from 4 meV from the commercially grown CVT crystal to 2meV from the flux grown crystal. Overall PL intensity from the flux grown monolayer was shown to be 100x greater than that from the commercial CVT¹⁷. The MoSe₂ monolayers used in this experiment were exfoliated exclusively from commercially grown CVT bulk single crystals.
3.2 Methods

3.2.1 Sample Fabrication

To isolate the effects of each treatment, we fabricate four samples: a bare monolayer on untreated SiO$_2$ surface, bare monolayer on an SiO$_2$ surface treated with a self-assembling monolayer (SAM), an encapsulated monolayer on untreated SiO$_2$ surface and encapsulated monolayer on treated SiO$_2$ surface. We used hexagonal boron nitride encapsulation and substrate surface passivation by SAM to minimize the effect of environmental variables.

Our BN-MoSe$_2$-BN stacks are assembled using the dry stacking technique outlined in Chapter 2. The BN flake thickness both above and below our monolayer is chosen to be between 20-30 nm. Encapsulation of samples in BN of this thickness serves to distance the sample from the local electrostatic environment of the substrate surface. In addition to physical separation from the substrate, BN itself is atomically flat and maintains an electrostatically neutral environment on its surface. Conversely, the SiO$_2$ substrate is prone to accumulation of electrostatic charges from dangling bonds and the adsorption of ambient molecules$^{19}$.

From Coulomb’s Law, the electrostatic field strength from the surface decreases by $r^{-2}$ where $r$ is the distance between stray charges and the monolayer. High quality, ultraflat and electrically neutral BN is used as a spacer to maximize this distance. Once the full stack is assembled on the PDMS/PC microlens, it is then transferred onto either a clean 285 nm SiO$_2$/Si substrate or one treated with a surface charge-passivated SAM. The SAM used in this work is the long chain alcohol dodecanol, which has a CH$_3$ group on one end and an OH group on the opposite end. The monolayer assembles itself such that the OH group of each molecule will form a hydrogen bond to the surface of the SiO$_2$. It can form these bonds because the SiO$_2$ surface is
imperfect, with some dangling bonds, stray charged particles and adsorbed molecules. Accordingly, the hydrophobic CH$_3$ group forms the top surface of the self-assembled monolayer. The end product comprises alcohol chains which are lined up vertically with respect to the SiO$_2$ surface with the CH$_3$ end facing out toward the environment.

3.2.2 Determination of Homogeneous Linewidth

Sample quality and environmental factors impact excitonic emission, but not all linewidth broadening comes from environmental factors. As discussed in Chapter 1, there exists a fundamental physical lower limit for a perfect crystal and this lower limit is linked to exciton dynamics in the sample. Using this relation and experimentally determined exciton lifetimes, the intrinsic minimum spectral broadening in excitonic emission. Specifically, the homogeneous linewidth $\gamma$ is given by the dephasing rate, which is the rate at which the ground state and excited state wavefunctions become out of phase:

$$\gamma = \frac{\Gamma}{2} + \gamma^*$$

where $\gamma^*$ is the pure dephasing rate from exciton-exciton and exciton-phonon interactions and $\Gamma$ is the exciton population relaxation rate. The latter is related to exciton lifetime, $T_1$, by $\Gamma = \frac{h}{T_1}$ while the former is related to coherence time, $T_2$, by $\gamma = \frac{h}{T_2}$. From measured spectra, $\gamma$ is half of the FWHM of a completely homogeneously broadened emission peak. Moody and Jacobczyk et al. both demonstrate that $\gamma^* \to 0$ for low temperature and low excitation density. For varying temperature, they measure both $T_1$ and $T_2$ and calculate $\gamma$. Extrapolating to low temperature, they determine in this limit, $2T_1 \cong T_2$. From the previous equations, they conclude $\gamma^* \approx 0$ and homogeneous linewidth can be calculated using the following equation$^{44, 45}$.
Coherence time measurements on an encapsulated MoSe$_2$ sample on a non-passivated substrate show an exciton coherence time of $T_2 = 0.98$ ps, which corresponds to a homogeneous linewidth of $\gamma = 0.601$ meV. From this, we expect a sample with purely intrinsic emission to produce a Lorentzian emission peak with a FWHM of 1.202 meV.

### 3.2.3 Measurement Techniques

We perform photoluminescence measurements at 3.8 K in a closed-system liquid helium cryostat with a piezo-scanning stage for precision mapping (Attocube Attodry 1100). Bandpass filters are used to isolate emitted photons with energy $\pm 10$ nm from either the neutral exciton or trion peak emission energies. A silicon APD is used to count the number of photons within that energy range emitted during the integration window. To generate a map, the number of counts is then assigned to a certain pixel corresponding to the coordinates of the stage during measurement. This was carried out for a given range of stage coordinates resulting in a map of the sample in which color intensity corresponds to PL emission intensity of the energy of interest. The pixels defining the sample region are determined on the PL map from emission characteristics and comparison with optical images of the sample. The count values from only this subset of pixels are used in statistical analysis.

### 3.3 Results

Photoluminescence spectra and integrated PL intensity maps are measured on each sample at cryogenic temperatures and can be seen in Figure 3.1 and 3.2. The bare monolayer on an untreated SiO$_2$ surface is shown in Figure 3.1(a) and exhibits about equal intensity of exciton
and trion PL emission with an exciton emission peak full-width-half-maximum (FWHM) of 11 meV. Encapsulation with BN significantly reduces linewidth of exciton PL spectrum to about 3 meV, but has little effect on the exciton/trion ratio (Figure 3.1b). Surface passivation via SAM greatly reduces trion intensity by eliminating electron traps and thereby creating a more electrostatically neutral surface. This can be seen in the PL spectrum of the monolayer on an SAM-treated substrate, shown in Figure 3.1(c). The PL spectrum which most resembles the theoretical intrinsic limit is achieved when both SAM surface passivation and monolayer encapsulation are implemented, shown in Figure 3.1(d). This sample exhibits a 4 meV FWHM with very large exciton/trion intensity ratio indicating a relatively electrostatically neutral environment.

Sample homogeneity is determined through statistical analysis of the intensity of each data point (pixel) on each PL intensity map. PL intensity mapping uses bandpass filters to integrate PL emission in a narrow energy region around either the exciton resonance or the trion
resonance. The ratio of the exciton emission intensity values and trion emission intensity values is calculated for each data point in the map and statistics are analyzed over the whole sample area. Figure 3.2 shows mapped PL emission for four conditions: (a) exciton emission from a bare monolayer on an untreated surface, (b) trion emission from a bare monolayer on an untreated surface, (d) exciton emission from an encapsulated monolayer on an SAM-treated surface and (e) trion emission from an encapsulated monolayer on an SAM-treated surface. Complete PL spectra from three spots on each sample show both exciton and trion emission from a bare monolayer on an untreated substrate (Figure 3.2c) and an encapsulated monolayer on an SAM-treated surface (Figure 3.2f). Spatial PL intensity mapping shows homogeneous trion/exciton ratio about equal to unity throughout the unpassivated bare monolayer sample. This is very clear in the sample spectra shown in Figure 3.2(c). A roughly homogeneous trion/exciton ratio is also seen throughout the encapsulated and passivated sample, with the exception to this is one area with a very low exciton/trion ratio due to the presence of a gold alignment mark on the substrate, which can be seen as a dark spot in Figure 3.2(d) and bright spot in Figure 3.2(e).

Figure 3.2: Integrated PL intensity maps indicating exciton emission from (a) a bare monolayer on an untreated substrate and (d) an encapsulated monolayer on a treated substrate; trion emission from (b) a bare monolayer on an untreated substrate and (e) an encapsulated monolayer on a treated substrate; PL spectra from points indicated in (a) are plotted in (c) and spectra from points indicated in (d) are plotted in (f).
Figure 3.3 shows histograms depicting the prevalence of PL intensity and trion/exciton ratio intensity values throughout the PL intensity maps. These histograms were made by counting the number of pixels in the PL intensity map for a given condition with a certain normalized intensity (a,c) or trion/exciton ratio (b,d) value. The largest inhomogeneity of PL intensity is seen on the bare MoSe$_2$ sample without surface passivation, shown in dark blue in Figure 3.3(a). The distribution of PL intensity values for this sample has a standard deviation of 40±10%. The variation halves with the addition of surface passivation and BN encapsulation to 19±2%, shown in light blue in Figure 3.3(c). Surface passivation has the most dramatic impact on the distribution of trion/exciton ratio values throughout a single sample. Passivation reduces variability from 1.2±0.3 for an untreated bare monolayer to 0.4±0.2 for a passivated bare monolayer (Figure 3.3b). Addition of BN encapsulation to the passivated sample further reduces the trion/exciton ratio to 0.18±0.06, which can be seen in Figure 3.3(d). This indicates the monolayer resides in the most electrostatically neutral environment of the four environments observed. The encapsulated MoSe$_2$ monolayers on a passivated substrate produce the most homogeneous PL intensity maps and trion/exciton ratio maps.

![Figure 3.3: Histograms showing prevalence of normalized intensity values in (a) and (c) or trion/exciton ratio values in (b) and (d) from PL mapping.](image)
Homogeneous versus inhomogeneous spectral broadening of the PL emission is determined through lineshape analysis. As discussed in Chapter 1, homogeneous spectral broadening is an intrinsic property of a material related to the carrier relaxation time and dephasing rate. As described in Chapter 1, it has been well established that this type of broadening results in a Lorentzian emission lineshape\textsuperscript{14, 19, 45, 46}. In section 3.2.2, the theoretical minimum FWHM of excitonic emission for this sample is predicted to be 1.202 meV.

Inhomogeneous spectral broadening can be caused by perturbations in the local lattice environment, including defects, strain, and electric fields, as discussed in Chapters 1 and 3\textsuperscript{14, 19, 45, 46}. The contribution from this type of broadening to the overall PL linewidth correlates to the deviation of the lineshape from intrinsic. Inhomogeneous broadening results in a Gaussian distribution in PL emission due to the random nature of the perturbations from which it occurs. The lineshape of real photoluminescence emission is broadened by a combination of homogeneous and inhomogeneous effects. A Voigt function is a convolution of Gaussian and Lorentzian lineshapes and is used to fit the PL spectra. The Lorentzian distribution is given as

$$L(x) = \frac{2A}{\pi} \left[ \frac{\omega_L}{4(x-x_C)^2 + \omega_L^2} \right]$$

where $A$ is the area of the curve, $\omega_L$ is the half-width-half-maximum and $x_C$ is the curve center. The Gaussian function is given as

$$G(x) = \frac{A}{\omega_G} \sqrt{\frac{2}{\pi}} e^{-\frac{-2(x-x_C)^2}{\omega_G^2}}$$

where similarly $A$ is the area of the curve, $\omega_G$ is the width of the curve defined as half the standard deviation and $x_C$ is the curve center. The Voigt function therefore is given by
\[ V(x) = y_0 + \int_{-\infty}^{\infty} G(x')L(x-x')dx' \]  

\[ V(x) = y_0 + \frac{A2ln(2)}{\pi^2} \left( \frac{\omega_L}{\omega_G} \right)^2 \frac{e^{-x^2}}{\sqrt{\ln2} \left( \frac{\omega_L}{\omega_G} \right)} \left( 2\sqrt{\ln2} \frac{x-x_G}{\omega_G} \right)^2 dx' \]

From this equation the FWHM of the contributing Gaussian and Lorentz functions can be found by

\[ w_G = \omega_G \sqrt{2\ln2} \quad \text{and} \quad w_L = 2\omega_L \]

Figure 3.4: (a) Representative PL spectra from an encapsulated monolayer on a treated substrate. (b) and (c) show example Voigt function fits to the exciton emission peak.

Representative spectra taken from encapsulated monolayers on a passivated substrate are shown on a logarithmic scale in Figure 3.4(a). Exciton peak location is shown to be relatively constant at 1.6391 eV with four spectra showing a redshift of 0.003 eV, which we attribute to local strain. The exciton peaks in all ten spectra were fit to a Voigt function. Two representative
spectra and their fits are shown in Figure 3.4(b) and (c). The linwidths due to the Lorentzian ($w_L$) and Gaussian ($w_G$) contributions are extracted. The average total FWHM of the sample is found to be $2.0\pm0.2$ meV with Lorentzian linwidths averaging $1.43\pm0.08$ meV and Gaussian linwidths averaging $1.1\pm0.3$ meV. The most narrow FWHM is measured to be $1.7\pm0.3$ meV. This is the closest to intrinsic observation of exciton PL emission from a monolayer TMDC at the time of this work.
CHAPTER 4

Charge Transfer Exciton Characterization

4.1 Introduction

Extensive work has been accomplished characterizing the behavior of excitons in single monolayer TMDCs, but charge transfer exciton behavior has been difficult to study. Charge transfer had been first discerned in TMDC heterostructures in 2014 by Hong et al. and Ceballos et al. Though no PL emission was detected, quenching of the intralayer PL emission suggests the carriers had diffused into different layers. Charge transfer emission was not seen either due to the momentum matching requirement for photon emission no longer being met or defect states providing a more favorable non-radiative recombination pathway\textsuperscript{20, 24}.

Photoluminescence emission from interlayer exciton recombination was reported by Rivera et al. in 2015\textsuperscript{22}. Though they made no effort to align the monolayers in momentum space, their MoSe\textsubscript{2}-WSe\textsubscript{2} heterostructure showed broad PL emission at 1.35 eV at both cryogenic and room temperatures. Using time resolved photoluminescence spectroscopy, the CT exciton was measured to have a lifetime of 1.8 ns\textsuperscript{47}. This is an order of magnitude longer than intralayer excitons, but two orders of magnitude shorter than theory predicts\textsuperscript{8}. Proper alignment of constituent monolayer crystal lattices will increase charge transfer efficiency between the layers. Source crystals grown using the flux method with very low defect density discussed in Chapter 3 will reduce non-radiative recombination pathways and scattering probability. By implementing both these improvements, we aim to fabricate high quality heterostructures.
In this experiment, we use clean fabrication techniques developed in Chapter 3 in combination with low defect density flux-grown TMDCs to fabricate several lattice-aligned MoSe₂-WSe₂ heterostructures encapsulated in BN. Charge transfer exciton behavior is characterized using static photoluminescence and TCSPC techniques. These devices exhibit strong charge transfer photoluminescence emission, efficient charge transfer and two orders of magnitude longer lifetimes than have previously been reported.

4.2 Methods

4.2.1 Stacking Technique

As previously discussed, theory indicates charge transfer exciton emission can only occur at low temperatures if the layers are aligned within ~5°. Therefore, precision in device fabrication is essential. I develop a stacking procedure for precise alignment and minimization of alignment error. A straight edge of the monolayer flake is measured using image processing software ImageJ; it provides a reference direction for further measurements. A reference is needed because ImageJ measures the angle between a defined direction and the horizontal in the image. In order to accurately discern the armchair direction as seen on the transfer stage, it must be measured in the reference frame of the sample rather than the reference frame of the image captured on the SHG measurement setup. Figure 4.1(a) and (b) show the measured armchair direction (white arrows) and the chosen reference direction (red arrows) in the orientations measured in the SHG setup. Figure 4.1(c) depicts a composite image of the heterostructure to be fabricated using these constituent monolayers in the frame of the transfer stage. The reference directions for both monolayers are measured on the transfer stage and lattice orientation is determined with respect to these directions. Using a rotational stage with <1° precision, the
position of each monolayer is adjusted to precisely align it relative to the other during the stacking process.

![Image showing WSe2 (a) and MoSe2 (b) monolayers](image)

Figure 4.1: WSe2 (a) and MoSe2 (b) monolayers. The lattice armchair direction found using SHG is shown in white arrow. Red arrows mark the reference direction which can be directly measured from an image. (c) Shows a composite image in which the monolayers in (a) and (b) are crystallographically aligned.

4.2.2 Measurement Parameters

We perform photoluminescence measurements at 3.8 K in a closed-system Montana Instruments liquid helium cryostat. Heterostructures are optically pumped using a 532 nm CW diode laser using 10 μW. The sample temperature is adjusted via power applied to a heating element in the cryostat platform. Sample temperature is monitored by a thermocouple installed on the sample mount and maintained by the cryostat PID controller. TCSPC is performed using a 532 nm, 120 fs pulsed laser. A silicon APD is used to count the number of photons emitted during the integration window. Optical filters are used to isolate emitted photons with energy in the region of the charge transfer exciton as seen in the static PL spectrum. An 850 nm high pass filter blocks any high energy photons including intralayer exciton emission and stray pump laser light.
4.3 Results

Low temperature photoluminescence spectroscopy performed on the heterostructures described above reveals a strong emission at ~920 nm (1.34 eV). This emission energy agrees with previous reports of CT exciton wavelength, both experimentally measured and computed\textsuperscript{9, 21, 22}. This emission peak is seen only inside the heterostructure region. Close to the heterostructure edge, emission intensity decreases and disappears completely inside monolayer regions, as shown in Figure 4.2. In the monolayer regions, the PL spectra show the expected exciton and trion emission for the individual constituent TMDC. Quenching of the intralayer emission, which corresponds with the appearance of a strong CT emission, indicates efficient charge transfer occurring in the heterostructure. A very narrow FWHM of the CT exciton of 8.1 meV shows the heterostructures have much less environmentally caused broadening effects than previously reported, typically on the order of tens of meV\textsuperscript{21, 22, 28, 45}.

![Figure 4.2: (Left) PL spectra from various points on a crystallographically aligned heterostructure.](image1)

![Figure 4.3: (Right) TCSPC data of CT exciton emission for a range of excitation powers.](image2)

We perform time-correlated single photon counting (TCSPC) to determine the lifetime of the charge transfer exciton. TCSPC data from a representative sample using multiple excitation
powers can be seen in Figure 4.3. We assume a single exponential decay function as a model for fluorescence. A CT exciton lifetime ranging from 250 ns to 400 ns is extracted for multiple samples, varying with location and by sample. This lifetime value is in good agreement with a previous study by Nagler et al. investigating charge transfer exciton lifetimes in TMDC heterostructures, which measured CT exciton lifetime of 138 ns\textsuperscript{21}. However, theory has predicted interlayer exciton lifetimes in an ideal heterostructure on the order of microseconds\textsuperscript{9}. This means either there exists a phenomenon unaccounted for in CT exciton lifetime calculations or there are imperfections in our fabricated heterostructures which cause faster recombination. The single exponential decay functional form of the TCSPC data suggests a clean interface by lack of fast radiative recombination pathways such as defect states.

![Figure 4.4: PL spectra around the CT exciton resonance for temperatures 10K-40K.](image)

Photoluminescence spectra are measured for various temperatures from 10 K to 120 K and are shown in Figure 4.4. Emission intensity of the charge transfer exciton is observed to be stronger at 20 K than at 10 K and then to decrease continuously for temperatures above 20 K.
This is indicative of phonon assistance in the transition. The heterostructure is not perfectly aligned, but rather requires phonon interaction to overcome a small momentum mismatch between K points in the two layers. If the lattices were perfectly aligned, the CT exciton emission intensity would be expected to continuously decrease with increasing temperature as scattering decreases exciton lifetime, limiting the ability of an excited electron to diffuse into the opposite layer before recombining. At very low temperatures and small twist angles, this effect is not pronounced. Figure 4.5 shows the available momentum range for an excited electron in the MoSe\(_2\) layer of a heterostructure with momentum mismatch of \(\Delta k\). For low temperatures (dark green shaded area), the local energy band minimum accessible to the excited electron is located in the same TMDC layer in which it originated. As temperature increases, this momentum range expands and at certain combination of temperature and momentum offset (light green shaded area), the accessible momentum range is sufficiently large to include the local conduction band minimum in the opposite layer. In this case, charge transfer will occur.

![Diagram](image_url)

*Figure 4.5: Diagram of the available momentum range for an excited electron in the MoSe\(_2\) layer of a heterostructure with momentum mismatch of \(\Delta k\).*
We also observe a redshift in CT exciton emission energy with increasing temperature. In Figure 4.5, it can be seen that at small interlayer misalignment, increased temperature allows sections of the WSe$_2$ conduction band with lower energy to become accessible, resulting in emission linewidth broadening with temperature. Both the MoSe$_2$ and WSe$_2$ bandgaps are adjusted due to thermal expansion of the lattice itself. The wavefunction overlap between neighboring atoms reduces, causing the hybridized band structure to renormalize. The effective bandgap between the available WSe$_2$ conduction band minimum and the MoSe$_2$ valence band maximum is reduced.

The experiments presented in this chapter have confirmed with the use of our improved low defect density source crystals and precision lattice alignment, we can produce high quality heterostructures which exhibit strong CT PL emission and significantly longer CT exciton lifetimes than previously reported in literature. In the following chapters, these properties will be used to further explore intrinsic physics of charge transfer excitons in these structures.
CHAPTER 5

Electron-Hole Plasma Generation in
TMDC Heterostructures

5.1 Introduction

In the previous study, we were able to create high quality MoSe$_2$-WSe$_2$ crystallographically aligned heterostructures. The low defect density flux-grown monolayers in combination with precision fabrication techniques result in high intensity charge transfer PL emission and enable very long exciton lifetimes. We now exploit these features and the unique layer separation of these heterostructures to generate layer separated electron-hole plasmas. In addition to gaining a deeper understanding of carrier behavior in these structures, potential uses for charge separated plasmas include lasers, optical modulators and optically induced superconductors$^{39}$.

Our heterostructures have exhibited CT exciton lifetimes up to 400ns. Since electrons remain in an excited state for such a long period of time more excitons are generated than decay, creating a buildup. Interaction between large numbers of excitons confined to two dimensions will lead to the formation of the electron-hole plasma at sufficiently high excitation power, meaning the electrons in holes once bound together become free carriers. Plasmas like this have been seen in WS$_2$ electrons and holes are free carriers but coexist in the WS$_2$ monolayer, which remains macroscopically neutral. Charge-separated electron-hole plasmas have been realized through the use of ionic gating, requiring the application of an outside voltage. These studies also use ionic liquid or gel gates, which limits the temperature ranges which can be studied$^{48-51}$. However, to explore MoSe$_2$-WSe$_2$ excitonic systems, they must be studied under cryogenic
conditions, which is not possible by using ionic gates. In this work we demonstrate the formation of spatially separated exciton and hole plasmas in lattice-aligned MoSe$_2$-WSe$_2$ heterostructures through optical pumping. The transition from bound excitons to plasma states is characterized through PL, TCSPC and transient reflectance measurements$^{52}$.

5.2 Methods

5.2.1 Sample Preparation

The previously described flux grown WSe$_2$, in-house grown CVT MoSe$_2$ and BN are exfoliated to required thickness using the exfoliation technique described in Chapter 2. The clean aligned stacking technique outlined in the previous chapter is employed to fabricate precisely crystallographically aligned heterostructures of this high quality material. Two samples are fabricated: a "bright" stack which is found to have relative twist angle of $\theta=4\pm2^\circ$ relative to perfectly aligned K-K or K-K' position and a "dark" stack which is found to have a relative twist angle of $\theta=13\pm2^\circ$. The "bright" stack is labeled as such because it displays CT exciton emission at cryogenic temperatures; the dark stack lacks this emission. All samples are placed on clean 285 nm SiO$_2$/Si substrates.

5.2.2 Determination of Exciton Density

To probe the effect of high carrier density in the heterostructure, we must be able to accurately determine the density of excitons and carriers in the structure. Varying laser pump powers are used to generate different densities of excitons. In the case of pulsed excitation, the induced carrier density per pulse is calculated by

$$n_{pulsed} = \frac{P\sigma}{A_{rep}E}$$

[26]
where $P$ is the excitation power, $\sigma$ is the absorbance of the laser light by the sample, $A$ is the incident area, $f$ is the pulse repetition rate and $E$ is the incident photon energy. To calculate the number of carriers under continuous excitation, we also take into account both the excited carrier decay rate and the carrier-dependent absorbance. Because illumination is continuous, exited carriers decay back to their ground state at a rate of $\tau(n)$ as more are generated at a rate of $G(n)$ where $n$ is the number of carriers in the material at a given point in time. Therefore, in the steady-state, the instantaneous change in the number of carriers at any moment is given by

$$\frac{dn}{dt} = G(n) - \frac{n}{\tau(n)} = 0 \quad \text{or} \quad G(n)\tau(n) = n \quad [27]$$

Since the excited state decay rate is only dependent on the number of generated carriers and not on the generation rate of new carriers, we take the decay rate $\tau(n)$ for each $n$ in the CW regime to be the same as the decay rate $\tau_0$ in the pulsed regime for the same $n$ number of generated carriers

$$\tau_{\text{CW}}(n)|_{n_0} = \tau_{\text{pulsed}}(n)|_{n_0} = \tau_0 \quad [28]$$

We calculate $n_{\text{pulsed}}$ and measure its corresponding $\tau_{\text{pulsed}}(n)$, plot these against each other, and fit the resulting data to get the functional form of $\tau_{\text{pulsed}}(n)$. Similarly, carrier generation rate under CW excitation is $G(n) = \frac{P \sigma(n)}{A\nu}$ where $\nu$ is the energy of incident photon. $\sigma(n)$ is calculated using the method outlined in the following section. Using these functional forms, we plot $G(n_{\text{eh}})\tau(n_{\text{eh}})$ for various pump power densities, $P$, where $n_{\text{eh}}$ is the electron/hole density. Each pump power produces the carrier density $n_{\text{eh}}$ point on its own curve which satisfies $G(n_{\text{eh}})\tau(n_{\text{eh}}) = n_{\text{eh}}$. From that, we now have a series of pump powers with their corresponding steady-state carrier density, $n_{\text{eh}}$. Plotting these values in Figure 5.1, we predict the resulting carrier density for a given pump power density.\textsuperscript{52}
5.2.3 Determination of Mott Threshold

As the buildup of excitons becomes sufficiently large, the Coulomb interaction between carriers becomes increasing screened until the binding energy of bound pairs reduces to zero. At this point, bound electrons and holes no longer "see" each other and are free carriers. The transition from a collection of bound excitons to dissociated free carriers is called the Mott transition and the carrier density at which it occurs is the Mott threshold.\(^{39}\) The Mott threshold is the carrier density at which the exciton density is sufficiently high to allow dissociation of electrons and holes into free carriers. The spectral feature indicative of this threshold is bleaching of the excitonic resonance in absorption spectra. An initial estimate of the Mott threshold \(n_{\text{Mott}} = 1.6 \times 10^{12} \text{ cm}^{-2}\) is found using \(a_0 n_{\text{Mott}}^{1/2} \approx 0.25\) as outlined by Meckbach et al. where \(a_0\) is the separation between the monolayers.\(^{53}\)

For a more accurate calculation, the Wannier equation\(^{29}\), which is a generalization of the semiconductor Bloch equations in the limit where all carriers are bound electron-hole pairs is used to calculate optical absorption spectra for the experimental parameters. The calculation
assumes a high excitation density but a quasi-thermal equilibrium. The Wannier equation must therefore be modified with expressions for renormalized electron-hole pair energy ($\varepsilon_A$) and Coulomb-screened potential ($V_{eff}$). These terms describe the many-body interactions between electron-hole pairs in high density. The solutions to this equation, $\phi_A^R(k)$, define the allowed exciton states\textsuperscript{54}.

$$\varepsilon_A\phi_A^R(k) = \varepsilon_A^{\pm}\phi_A^R(k) - \sum_{k'}V_{eff}\phi_A^R(k')$$  \hspace{1cm} [29]

We use the solutions to the Wannier equation to solve for macroscopic polarization of the sample material. From there, the linear electric susceptibility is calculated and used to further calculate transmission and reflection spectra. Absorption is found using:

$$A(\omega) = 1 - R - \left(\frac{n_{Si}}{n_{air}}\right)T$$  \hspace{1cm} [30]

where $R$ is reflectance, $T$ is transmittance, and $n_{Si}$ and $n_{air}$ are the indices of refraction of Si and air respectively. Calculated differential reflectance spectra for different excitation powers are plotted in Figure 5.2(a). The measured reflectance at similar excitation powers is plotted in Figure 5.2(b) and correlates well to the calculated spectra.

From these calculated values of reflectance, we compute absorption spectra over a wide range of excitation density. Calculated absorption over two orders of magnitude excitation power are plotted in Figure 5.2(c). We take the Mott threshold to be the excitation density for which the resonance peak of the MoSe$_2$ vanishes. By examining calculated absorption spectra, we determine this occurs at $n = 3 \times 10^{12}$ cm$^{-2}$ and determine this to be the Mott threshold.
5.3 Results

Photoluminescence measurements are carried out at 4 K in vacuum and a CW diode laser at 532 nm is used as an optical pump. Figure 5.3(a) shows PL spectra from a range of pump powers on the aligned heterostructure sample. Optically pumping the sample with different laser powers creates varied exciton densities in the sample; the densities are calculated using the method described above. Displayed in the inset of Figure 5.3(a) are MoSe$_2$ and WSe$_2$ PL spectra for separate monolayers, showing the neutral exciton (XM) and trion peaks for MoSe$_2$ and the neutral exciton (XW) peak and other peaks assigned to the trion and other multibody states typical of low defect WSe$_2$ monolayer PL$^{55}$. A color contour plot of normalized PL intensity under CW excitation is shown in Figure 5.3(b). Solid lines define the FWHM of the CT exciton peak. Dashed lines indicate 75% (inner) and 25% (outer) of the maximum PL intensity. From this plot, it is clear the FWHM of the CT emission peak drastically increases once the Mott
threshold is surpassed. The integrated PL intensity of the CT exciton emission peak in the bright sample and of the intralayer exciton emission peaks for both the bright and dark samples are found and shown in Figure 5.3(c). The FWHM of the CT exciton peak is also found and shown in Figure 5.3(d). The dotted line denotes the predicted Mott threshold, above which forms an electron-hole plasmas as described above. Below this threshold, the intralayer exciton emission is completely quenched. Above the threshold, the interlayer emission peak broadens and the intralayer emission appears. This increase in FWHM by up to a factor of four signifies the elimination of bound-state excitons in this regime and confirms the theoretical prediction for Mott transition carrier density. Excitons no longer remain bound and instead dissociate into free carriers, introducing a larger spread in the emission energies.

![Figure 5.3](image)

Figure 5.3: (a) PL spectra for various excitation densities. Inset: WSe2 and MoSe2 intralayer exciton PL spectra. (b) Contour map of heterostructure PL spectra near the CT exciton emission. (c) FWHM of the CT exciton emission over four orders of magnitude excitation density. (d) Integrated PL intensity for the CT exciton, and intralayer exciton in both bright and dark samples over four orders of magnitude excitation density. (d) The probability of both an electron and a hole occupying the K-point for creation of a CT or interlayer exciton.
The appearance of intralayer exciton emission above the Mott threshold can be explained by charge buildup in each layer. The accumulation of free charge carriers creates a voltage across the interface which eventually overcomes the 300 meV offset between the conduction (valence) bands of the two materials. At this point, the Fermi level is situated in the conduction bands, eliminating the type II band alignment which drives charge transfer. This allows repopulation of the conduction (valence) band of WSe$_2$ (MoSe$_2$) and creates a population inversion at the band edge$^{39, 53}$. We calculate the carrier density to for this phenomenon to occur by modeling the heterostructure as a parallel plate capacitor. The necessary electric field ($\vec{E}$) needed to overcome the voltage of 300mV is:

$$V = |\vec{E}|d = \frac{\rho}{\varepsilon}d$$

[32]

where $d$ is interlayer spacing (6.5Å) and $\varepsilon$ is the vacuum permittivity. The charge density is given by $\rho$ and can be defined in terms of the carrier density and elementary charge:

$$\rho = nq$$

[33]

Using these values, we calculate the carrier density needed to overcome the band offset is $n = 2.5 \times 10^{12}$ cm$^{-2}$, which is about the same as our predicted Mott threshold of $n_{\text{Mott}} = 3 \times 10^{12}$ cm$^{-2}$. A diagram of this mechanism can be seen in Figure 5.4. The resurgence of intralayer exciton PL emission can also be seen in the dark sample, in which the CT exciton transition is non-radiative.
Figure 5.3(d) shows the calculated probability of simultaneously finding electrons and holes in the K-valleys of either WSe$_2$ or MoSe$_2$. Because this is the condition required for interlayer recombination to occur, the calculated probabilities serve as a theoretical prediction of PL emission source at different excitation densities. The only predicted source of emission below an excitation density of 10$^{13}$ cm$^{-2}$ is CT exciton recombination. Above ~10$^{13}$ cm$^{-2}$, the probability of emission from the intralayer MoSe$_2$ exciton becomes non-negligible, followed by that of the intralayer WSe$_2$ exciton at ~10$^{14}$ cm$^{-2}$. Therefore, this calculation accurately predicts the appearance of emission peaks at high excitation densities seen in Figure 5.3(c).
Figure 5.5: TCSPC data from CT exciton emission at various excitation densities. (b) PL spectra near the CT exciton resonance (c) CT exciton lifetime for various carrier densities.

We perform TCSPC using a pulsed 532 nm pump laser with pulse width of 150 fs and integrate over the energy range 1.2-1.5 eV. The data show the decay of CT exciton population with time for excitation densities ranging from $10^{10}$ to $10^{14}$ cm$^{-2}$. PL spectra of the CT exciton emission from which the TCSPC data in Figure 5.5(a) was taken is shown in Figure 5.5(b). The TCSPC data are fit using exponential decay functions and the extracted decay time constants are plotted against carrier density in Figure 5.5(c). For low excitation densities, a single exponential decay function best fits the data and is indicative of exciton emission from low-defect material. Time constants in this regime are in the range $\tau_0 = 200\pm40$ ns, characteristic of long-lived charge transfer excitons. Approaching and above the Mott density, decay becomes multiexponential. For data requiring a multiexponential fit, the shorter lifetime is plotted as plasma recombination has been shown to occur on shorter timescales than exciton recombination$^{38, 42, 53}$. 

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Transient reflectance spectra for a range of excitation densities both below and above the Mott transition are shown in Figure 5.6(a) through (d). Transient reflectance spectra at different pump-probe delay times for the lowest and highest excitation densities are shown in Figure 5.6(e) and (f). Panels (a) and (b) show photo-bleaching peaks (blue) at ~1.63 eV and ~1.7 eV attributed to Pauli Blocking of the individual MoSe$_2$ and WSe$_2$ monolayer intralayer transitions$^{11}$. As mentioned in Chapter 2, photo-bleaching signatures in reflectance spectra are indicative of a large population of excited state electrons, which becomes more pronounced with higher excitation densities. In panel (e), reflectance contrast spectra at low excitation density at several times after excitation clearly show photo-bleaching dips at the intralayer exciton
resonances. Below the bandgap, including at the charge transfer exciton resonance, there are no optical features.

At higher excitation density in panels (c) and (d), we see broad photo-induced absorption features (red) below 1.6eV and, for very high pump power, just above each exciton resonance energy. This feature is characteristic of plasmonic emission due to bandedge population inversion. The effect becomes more pronounced and reaches lower energies as excitation power increases and bands continue to fill. Figure 5.6(f) shows reflectance contrast spectra at high excitation density at several times after excitation. The induced absorption signature below the exciton resonance is clearly present until 100 ps after excitation. Panels (g) and (h) show PL intensity at the CT exciton and MoSe₂ exciton resonance respectively over time for different pump powers. At low pump powers, slight photo-bleaching is seen at the CT exciton resonance, while a much larger photo-bleaching occurs at the MoSe₂ exciton resonance. This difference is due to the much lower oscillator strength of the CT exciton as compared to intralayer excitons. For very high excitation densities, the reflectance contrast at the MoSe₂ exciton resonance does not increase to the point of becoming a positive transient reflectance signal, but it does indicate there is some emission which is competing with the bleaching phenomenon.
CHAPTER 6

Enhancement of PL Emission Through Gold Nanorod Plasmon Coupling

6.1 Introduction

Due to their direct bandgaps in the visible regime, TMDCs are of great interest for use as new low power consumption commercial devices such as displays and LEDs. However, the emission efficiency of TMDCs is currently far too low for commercial applications. Emission enhancement through coupling of excitons with plasmonic nanostructures has shown great promise for quantum wells, quantum dots, LEDs and fluorescent molecules\textsuperscript{31-37, 56-60}. Plasmonic coupling with excitons has yet to be realized for enhancement of emission in TMDC heterostructures. The ability of these materials to couple with plasmonic structures has potential uses in plasmonic circuits, sub-diffraction limited imaging. In this study, we apply gold nanorods onto our crystallographically aligned MoSe\textsubscript{2}-WSe\textsubscript{2} heterostructures. The gold nanorods have been fabricated such that their longitudinal surface plasmon mode is resonant with the CT exciton energy. We probe characteristics of enhanced CT exciton emission through static low temperature and temperature dependent PL spectroscopy, TCSPC and PL mapping.

6.2 Methods

6.2.1 Gold Nanorod Properties

Since the physical boundaries of the nanorods confines and therefore quantizes normal modes of the surface plasmon, their size and geometry determine their surface plasmon resonances. We have acquired gold nanorods of diameter 21±5 nm and length 122±23 nm. The absorbance spectrum of these nanorods is seen in Figure 6.1 along with the PL emission
spectrum of the CT exciton. From the absorbance spectrum, we see a resonant mode at 1.31 eV, corresponding to the longitudinal surface plasmon mode. There is an additional resonance at ~2.5 eV corresponding to the transverse surface plasmon mode. The CT exciton resonance occurs at 1.34 eV, very close to the nanorod resonance and where the nanorods exhibit >90% absorbance. Our pump laser resonances are at 532 nm (2.33 eV) and 680 nm (1.82 eV), where nanorod absorbance just under 20% and 10% respectively. Because of this we know absorption of the pump laser by either nanorod resonant mode is minimal.

The gold nanorods are suspended in methanol, with a concentration of 10 mg/mL. To ensure even distribution of nanorods in the liquid, the suspension is mixed using a vortex mixer for 3 minutes before application. To apply the nanorods onto a sample, the heterostructure on SiO₂ chip is cleaned by soaking in chloroform for at least 30 minutes. The chip is then spun at 2500 rpm and 0.1 mL of methanol/nanorod suspension is drop-cast onto it. The chip is kept spinning for 2 minutes after application of the nanorod suspension to allow for evaporation of the solvent. The sample is then rinsed in ethanol to remove any residue. Scanning electron
microscopy used to verify successful application of nanorods (Figure 6.2). We determine an average coverage of 8 nanorods/μm².

Figure 6.2: SEM micrograph of gold nanorods deposited on SiO₂ substrate.

6.2.2 Sample Geometry

Three heterostructure samples fabricated using the clean stacking technique outlined in Chapter 2 and the crystallographic alignment techniques outlined in Chapter 4. We fabricated our heterostructures with the top BN thicknesses of 15, 17 and 20 nm, which act as an insulating spacer between the heterostructure and the nanorods. The distance between nanorods and emitting material effects coupling strength³²,⁵⁹. Kumar et al. found a r⁻⁴ dependence on coupling strength between the nanorods and emitting material due to the enhanced electric field strength dropping off with distance⁵⁹. However, if the distance between the plasmonic metal structure and emitting material is too small or nonexistent, Förster resonant energy transfer (FRET) will overtake radiative recombination as the dominant recombination pathway. FRET it a mechanism of resonant dipole-dipole coupling which transfers energy from an electron in an excited state to one in a ground state without the emission and subsequent absorption of a photon. The coupling strength between particles in this mechanism follows a r⁻⁶ dependence and is therefore only non-
negligible for very short distances. If the nanoparticles and our emissive layer become close enough for FRET to occur, emission will be quenched rather than enhanced\textsuperscript{32, 59}. Pan et al. found a balance between minimizing FRET and maximizing coupling between their gold nanoparticles and quantum dot arrays to be a separation of 15 nm\textsuperscript{32}. Further, Yeh et al. see PL enhancement even with a plasmonic silver grating separated from quantum well emitters by 80 nm\textsuperscript{37}. They claim this distance is still within $e^{-1}$ drop in the enhanced electric field strength from surface plasmons induced in the metal and therefore coupling is still possible. The bottom BN in these samples is maintained as our standard 25-30 nm thickness to isolate the heterostructure from substrate electrostatics, as discussed in Chapter 3.

6.2.3 Measurement Details

We perform photoluminescence measurements at 3.8 K in a closed-system liquid helium Montana Instruments cryostat. Heterostructures are optically pumped using a 532 nm CW diode laser using 2 $\mu$W and 10 $\mu$W pump power. These powers were chosen to maximize the signal without saturating the spectrometer. We determine using the measured CT exciton lifetime and procedure outlined in the previous chapter that the Mott threshold is reached at 10 $\mu$W. We stay below this threshold to ensure we are probing the characteristics of the charge transfer exciton rather than dissociated charge carriers. The sample temperature is adjusted by power applied to a heating element in the cryostat platform and is monitored by a thermocouple installed on the sample mount and maintained by the cryostat PID controller. TCSPC is performed using a 680 nm, 150 fs pulsed laser. A silicon APD is used to count the number of photons emitted during the integration window. Optical filters are used to isolate emitted photons with energy in the region of the charge transfer exciton as seen in the static PL spectrum. An 850 nm high pass filter blocks any high energy photons including intralayer exciton emission and stray pump laser light.
A galvo mirror system is used to scan the pump beam over the sample surface. To generate a map, the number of counts is then assigned to a certain pixel corresponding to the location upon which the laser is incident for the measurement. This was carried out for a given scanning range resulting in a map of the sample in which color intensity corresponds to PL emission intensity of the energy of interest.

6.3 Results

Emission enhancement is determined as the ratio between maximum PL intensity for a given pump power and integration time for the sample with nanorods and without. Maximum enhancement of PL emission is found to be 49x the initial PL intensity. Spectrum from this sample can be seen in Figure 6.3. In addition to the strong CT exciton peak, Figure 6.3 shows a distinct lack of intralayer exciton emission, indicating efficient charge transfer between the monolayers. The largest enhancement was found in samples with the lowest initial PL emission intensity. In Figure 6.4, this trend can be seen through three separate heterostructure samples studied here. Though our source material is known to have very low defect density as-grown, the fabrication process can introduce defects and residue which can interfere with charge transfer exciton creation and subsequent recombination. Assuming the primary cause of low CT exciton emission from a heterostructure is defects rather than crystallographic misalignment, we believe the addition of the nanorods creates a radiative recombination pathway more favorable than defect-mediated non-radiative recombination.
Photoluminescence intensity mapping is performed on an aligned heterostructure before and after application of nanorods. Intralayer PL intensity over the sample is shown in Figure 6.5(a) without nanorods and (b) with nanorods. Similarly, charge transfer PL intensity is shown in Figure 6.5(d) without nanorods and (e) with nanorods. By comparing the emission at these two resonances, we see the CT emission is confined to the heterostructure region while the intralayer emission is seen in regions with only the MoSe$_2$ monolayer. Figures 6.5(c) and (f) show the change in PL intensity at these resonance energies with the application of nanorods. We can see in panel (f) the most enhancement of emission at the CT resonance occurs in regions which had very low initial emission at this energy. Locations with initial high CT exciton emission remain relatively unchanged.

From figure 6.1 we know that the exciton resonance energy (1.34 eV) differs slightly from the nanorod resonance (1.31 eV). Figure 6.6 shows the emission enhancement and the initial CT emission energy deviation from the nanorod resonant energy. We can see the locations

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**Figure 6.3:** (Left) PL spectra from aligned heterostructures with (black) and without (red) gold nanorod application.

**Figure 6.4:** (Right) PL emission enhancement at the CT exciton resonance compared to the CT exciton PL emission intensity at the same location before the application of nanorods.
which initially exhibited CT emission closer to the nanorod resonant energy experienced greater enhancement than those emitting at energies farther away.

The change in CT emission energy with and without nanorods at low temperature is shown in Figure 6.7. The dark red line indicates the points where these two values are equal. The average CT emission energy before the application of nanorods is 1.334±0.009 eV while with nanorods the average emission energy is 1.335±0.006 eV. Based on this, we can see the application of nanorods has no appreciable effect on emission energy.

Figure 6.5: PL mapping showing the intralayer PL intensity with (b) and without (a) nanorods, and the CT exciton PL intensity with (e) and without (d) nanorods. The change in emission intensity for the intralayer (c) and interlayer (f) excitons are also shown.
Figure 6.6: PL emission enhancement of the CT exciton emission based on the initial emission energy deviation from the nanorod resonance energy.

Figure 6.7: Emission energy of the charge transfer exciton with and without nanorods. The dark red line indicates where these two values are equal.

Static PL measurements are taken at various temperatures up to room temperature. Figure 6.8 shows the CT emission energy for both samples with (red) and without (black) nanorods from low to high temperature. We can see both samples follow the same trend regardless of the addition of nanorods, indicating the nanorods have no effect on bandgap renormalization. Since the CT emission persists to higher temperatures, we can see the emission energy continues to reduce with increasing temperature to 1.27 eV at room temperature.

Figure 6.8: Charge transfer exciton emission energy from 4 K to room temperature.

Figure 6.9: Room temperature PL emission spectrum of aligned heterostructure with gold nanorods.
Room temperature PL spectra is shown in Figure 6.9. We see that some CT exciton emission persists to high temperature. Residue between layers and any lattice defects or dopants introduced during the fabrication process serve as scattering sites and non-radiative recombination centers, preventing charge transfer and quenching CT exciton emission. Maintaining CT emission to room temperature is a good indication that the interface between monolayers is clean and the fabrication process has not significantly degraded the crystal quality. Emission from intralayer transition is much stronger than that from the interlayer transition, indicating that charge transfer is not occurring as efficiently compared to low temperature. This is to be expected as scattering events are much more prevalent at higher temperatures; this same trend occurs for intralayer emission at high temperature.

![Image](image.png)

**Figure 6.10:** PL emission intensity for heterostructures with (red) and without (black) gold nanorods from 4 K to room temperature.

**Figure 6.11:** CT exciton PL emission enhancement from 4K to room temperature.

The maximum PL intensity seen in heterostructures with (red) and without (black) nanorods from 4K to room temperature is seen in Figure 6.10. We can see a large drop in intensity from the sample with nanorods from 4 K to ~100 K. The calculated enhancement in this temperature range is shown in Figure 6.11 and shows a reduction in enhancement from 5.1 to
3.4. This could be a result of scattering events which become increasingly prevalent with temperature.

The question we must now answer is: what is the physical mechanism behind the observed emission enhancement? Current literature attributes an increase in exciton emission intensity with the addition of nanoparticles or plasmonic metal gratings to the Purcell effect. As was discussed in Chapter 1, the Purcell effect is an increase in radiative recombination rate due to localized electric field enhancement in the near-field. A signature of this phenomenon is increased rates of absorption and emission. To determine if this is also a possible mechanism responsible for the CT exciton PL enhancement, we perform TCSPC measurements.

![TCSPC data](image)

**Figure 6.12:** TCSPC data from the same location with (red) and without (black) nanorods.

**Figure 6.13:** Measured CT exciton lifetime with nanorods against without nanorods.

Example TCSPC spectra from the same location on an aligned heterostructure with (black) and without (red) nanorods are shown in Figure 6.12. The TCSPC data are fit using biexponential decay functions. Having a biexponential fit on TSPC data is indicative of disorder in the sample. Defects in the lattice can potentially serve as recombination centers, prompting exciton decay faster than in a pristine crystal. For this reason, the longer decay constant is taken
as the exciton lifetime while the shorter decay time is attributed to scattering events and defect-mediated recombination. Figure 6.13 shows the measured exciton lifetimes with and without the application of nanorods at the same locations on the sample. The red line indicates the same lifetime measured for both cases. We can see no appreciable change in exciton lifetime with the addition of nanorods. We therefore cannot conclude that the Purcell effect is responsible for the enhancement of CT exciton PL emission.

Though we do not see the drop in exciton lifetime characteristic of the Purcell effect, we also cannot rule it out. As discussed in Chapter 4, the theoretical maximum lifetime of CT excitons is 1 μs, but the maximum lifetime we have measured in our samples is 400 ns. The emission decay rate is related to the lifetime by \( k = \tau^{-1} \) where \( \tau \) is lifetime.

There are two contributions to emission decay rate: the radiative decay rate, which is effected by intrinsic disorder such as defects; and the non-radiative decay rate, which is effected by extrinsic disorder from environmental sources as discussed in Chapter 3.

The overall emission decay rate from the lifetime measured with TCSPC is the sum of these two contributions, \( k = k_{rad} + k_{NR} \). We have found that the overall decay rate remains unchanged between the enhanced and nominal samples. However, the Purcell effect reduces the radiative decay rate only. It is possible that the radiative decay rate has actually decreased, but the non-radiative component dominates the overall decay rate. In this case, any change in radiative decay rate would be undetectable in TCSPC data. To determine if the radiative decay rate has decreased, we compare the relative quantum yield between the enhanced and nominal samples. The enhancement factor is used as the ratio between the absolute quantum yield of each of these
samples. Taking the relative quantum yield to be the maximum enhancement we have measured, 49, we get:

\[
QY_{Rel} = \frac{k_{rad}}{k_{rad} + k_{NR}} = \frac{\tau_{rad}^{-1}}{\tau_{rad}^{-1} + \tau_{NR}^{-1}}
\]

\[
49 = \frac{QY_{Au}}{QY_{Bare}} = \frac{\tau_{rad,Au}^{-1}}{\tau_{rad,bare}^{-1} + \tau_{NR}^{-1}} = \frac{\tau_{rad,Au}^{-1}}{\tau_{rad,bare}^{-1}} = \frac{\tau_{rad,bare}}{\tau_{rad,Au}}
\]

We see that for the same measured lifetime, the enhancement factor is the ratio between the radiative lifetimes of the enhanced and nominal samples. Therefore, the radiative decay rate in the enhanced sample has reduced by a factor of 49 compared to the nominal sample. This is a strong indication that the Purcell effect is occurring.

The non-radiative component dominating the overall decay rate indicates a significant amount of external disorder still remains in the sample. If we assume the nominal sample with the longest measured lifetime lacks any extrinsic disorder and the measured lifetime is purely radiative, we can use this measured value to calculate the purely radiative lifetime of the CT exciton in the enhanced sample:

\[
49 \tau_{rad,Au} = \tau_{rad,bare} = 400 \text{ ns}
\]

\[
\tau_{rad,Au} = 8 \text{ ns}
\]
We can see that for an enhanced sample with minimal extrinsic disorder, the CT exciton lifetime would be reduced from 400 ns to 8 ns.

An alternative possible mechanism for emission enhancement is that the gold nanorods provide some momentum to overcome the small lattice mismatch between the constituent monolayers. In order for radiative recombination to take place at low temperatures, the bound electron and hole must have very little difference in crystal momentum in order for momentum to be conserved after the emission of a photon. However, this condition does not necessarily need to be met for non-radiative energy transfer from the exciton to the gold nanorod surface plasmon. Once this energy transfer occurs, the momentum matching requirement no longer applies since surface plasmons emit photons through momentum-providing scattering events on the rough nanorod surface or at either end.\textsuperscript{31, 32, 34, 58}

We attempted to test this theory by applying nanorods to crystallographically unaligned sample. Measuring the previously defined reference angles on the completed heterostructure, we are able to determine that the lattice mismatch of a particular "dark" sample is \(\sim 13^\circ\). We refer to this sample as dark because it does not exhibit charge transfer emission. We compare PL from this sample to that of a "bright" sample which is measured to have a lattice mismatch of \(\sim 3^\circ\). Our dark sample not only does not exhibit charge transfer emission but only produces weak intralayer exciton emission. One reason for this could be that charge transfer is occurring, but the momentum matching requirement for photon emission is not met, and therefore the charge transfer excitons must recombine non-radiatively. This is our ideal scenario for using nanorods to induce emission in an otherwise dark heterostructure. However, once nanorods were applied to our dark sample, charge transfer emission was still nonexistent. This could due to insufficient coupling between the nanorods and heterostructure. We have not yet studied the effect of top BN
thickness on PL enhancement and this parameter could be optimized for maximal coupling and energy transfer between the heterostructure and the gold nanorod surface plasmons. Further experiments to elucidate the mechanism of PL emission enhancement are discussed in Chapter 7.
CHAPTER 7

Summary and Future Work

7.1 Conclusions

1. The local electrostatic environment is shown to have a major impact on the optical properties of TMDCs. In our experiment, BN encapsulation of MoSe$_2$ monolayers reduced disorder induced by the local electrostatic environment and greatly reduced the linewidth of the resulting exciton PL emission. Surface passivation with self-assembling monolayers reduced excess charge in the sample as demonstrated by greatly reduced trion PL emission. Using both techniques, we greatly improved the homogeneity of PL emission and improved the electrostatic environment across a given sample and achieved near-intrinsic PL overall linewidth of $1.7 \pm 0.3$ meV.

2. The clean stacking techniques developed in Chapter 3, lattice alignment and low-defect flux-grown material are employed to fabricate high quality TMDC heterostructures which demonstrate efficient charge transfer. Our heterostructures demonstrated strong CT exciton emission with narrow PL linewidth of 8.1 meV and consistently long lifetimes in the hundreds of nanoseconds, with a maximum exciton lifetime of 400 ns. These measured properties are a great improvement upon those of previously reported charge transfer excitons.

3. We exploited the long lifetime of charge transfer excitons in our crystallographically aligned heterostructures to create a buildup of excitons in the sample. Layer-separated electron-hole plasmas are demonstrated through optical pumping of these heterostructures and characterized by a sudden broadening of PL emission and drop in exciton lifetime above the Mott transition.
The emergence of a broad induced absorption feature in transient reflectance spectra above the Mott transition further supports this determination.

4. Coupling of charge transfer excitons to surface plasmon modes of resonant gold nanorods is demonstrated. We achieve up to 49x enhancement of charge transfer exciton PL emission with nanorods as compared to without. Due to this enhancement, CT exciton emission is able to persist to room temperature. Charge transfer exciton lifetime and emission energy are shown to be insensitive to the addition of the nanorods.

7.2 Future Work

7.2.1 Sample Inhomogeneity

In Chapter 4 we then demonstrated the use of clean fabrication techniques along with lattice alignment and incorporation of flux-grown crystals to greatly improve heterostructure quality and reveal charge transfer exciton behavior which more closely resembles their theoretical intrinsic behavior. The characteristics of the CT emission from these heterostructures still deviate significantly from predicted intrinsic behavior, though they do improve greatly. The lifetime of CT excitons in our heterostructures is measured to be in the hundreds of nanoseconds, but on a single sample that value ranged greatly from 200 ns to 450 ns. We also observe that PL emission from both intralayer and interlayer transitions vary greatly in intensity and somewhat in energy. Both of these features indicate disorder-induced sample inhomogeneity.
Mapping of PL emission unequivocally shows the inhomogeneity of our heterostructures. We tend to see strongest emission around edges and "bubbles," while emission occurs sporadically inside the bounds of an optically "clean" structure. "Bubbles" are areas in the sample which foreign material has become trapped between layers; they are visible optically. We see this effect clearly in Figure 7.1, which shows an optical image and PL intensity map of CT exciton emission in panels (a) and (b) respectively. Charge transfer exciton emission is greatest along the border between monolayer and bulk MoSe$_2$ areas. Emission is also strong at the corners of the heterostructure region while the interior of the heterostructure has a mix of bright and dark areas. The spatial dependence of PL emission intensity indicates this effect is not due to lattice mismatch. Our starting constituent monolayers have shown to be high quality with few defects. It is possible that defects could be induced in the sample during the fabrication process. Encapsulated monolayer samples fabricated using similar methods had been shown to be homogeneous in Chapter 3. A complication which is not experienced in emission from encapsulated monolayers is the requirement of coupling between layers. Any residue or defects at the interface between the monolayers not only acts to hinder charge transfer, but also acts as a
scattering site or center for non-radiative recombination. This makes CT exciton recombination inherently more sensitive to interfacial imperfections. Further study on maintaining clean interfaces and methods for more accurate lattice alignment are necessary to generate intrinsic charge transfer exciton emission.

7.2.2 Mechanism of Charge Transfer Emission Enhancement

In Chapter 6, we demonstrate significant enhancement of CT exciton PL emission in crystallographically aligned MoSe₂-WSe₂ heterostructures. The Purcell effect has been identified as the mechanism by which emission in enhanced in systems such as quantum wells, LEDs and fluorescent molecules. The identifying characteristic of the Purcell effect from these studies is the drastic decrease in excited state lifetime. Kwon et al. report a reduction in exciton recombination time in InGaN/GaN quantum wells by 62% with the addition of resonant silver nanoparticles. The corresponding exciton PL emission in their sample had increased 14-fold. From our measurements of charge transfer exciton lifetime, we see no change with or without the application of resonant nanorods. It therefore appears the Purcell effect is unlikely to be a substantial contributor to PL emission enhancement because we see no change to measured excitonic lifetimes.

The second possible mechanism for enhancement discussed in Chapter 6 was non-radiative energy transfer from the CT exciton to the resonant surface plasmon mode of the nanorods. In doing this, the nanoparticles create a radiative recombination pathway which bypasses a momentum matching requirement. We attempted to induce CT exciton emission from a "dark" misaligned sample to explore this option. No emission was seen, but further investigation is merited. The momentum offset between the materials is proportional to the
lattice twist angle between them. It is possible the lattice mismatch of the experimental sample used was too great for scattering events to compensate. The sample used in our experiment was misaligned by ~13° and theory suggests that CT emission occurs for twist angles less than ~5°. A precise twist angle dependent study at small lattice mismatch angles between these values could determine the limitations of momentum contribution from the addition of nanorods.

Additionally, coupling strength between the nanorod surface plasmon modes and CT excitons may have been too weak in the heterostructures studied. As previously discussed, Kumar et al. determined a r⁻⁴ coupling strength between an exciton and plasmonic structure with a resonant surface plasmon mode⁵⁹. This is a very strong dependence on the thickness of the insulating spacer between our emitting heterostructure and gold nanorods. As discussed in Chapter 6, for very thin BN, FRET emerges as a non-negligible non-radiative recombination pathway for CT excitons. FRET is a much faster process than exciton recombination, even if competing with the enhanced spontaneous emission rate caused by the Purcell effect. Though Pan et al. determined the optimal spacing between gold nanoparticles and an array of quantum dot LEDs to be 15 nm, Li et al. report FRET-dominant recombination of excitons in Cu₂O separated from gold plasmonic structures by 11 nm of insulating SiO₂.³²,⁶⁰ A study confirming the relationship between BN thickness and CT exciton PL emission enhancement in TMDCs could shed light on the nature of the coupling mechanism between them.

For very thick BN, addition of gold nanorods may result in reduced CT excitation PL signal. Though the gold nanorods used in our experiment are tailored to the CT exciton resonance to aide in coupling, this also means the gold nanorods have very high absorption at this resonance. If the spacing between the nanorods and the heterostructure is too large for coupling to take place, emission could be reabsorbed by the gold nanorods. A similar
phenomenon was seen by Yeh et al. with large spacing between fluorescent molecules and a silver plasmonic grating\textsuperscript{61}. Investigations into optimal spacing thickness between our heterostructures and gold nanorods are needed to determine if this is a prevalent energy transfer mechanism.

7.2.3 Twist Angle Dependent Charge Transfer Exciton Dynamics

Our study of TMD heterostructures started with the realization that any meaningful measurement of CT exciton characteristics required high quality constituent material, clean fabrication techniques and precise placement. Because we have been lacking in these prerequisites, are still lacking an angle-dependent study on CT exciton dynamics. As was discussed in Chapter 1, there only exists theory developed by Yu et al. indicating CT exciton emission within ±5° of alignment, but no experimental confirmation\textsuperscript{10}.

Our goal is to determine the dynamic behavior of CT excitons with varying momentum space misalignment between layers. To do this, we plan to develop a technique to rotate one TMD with respect to another using the tip of an AFM in contact mode. This will allow for very precise (sub-degree) relative positioning and eliminate sample to sample variation in our data. A major advantage of this technique is that it allows for the possibility of being able to turn CT exciton emission on and off depending on the position of the monolayers. Once these samples have been fabricated and we can reliably and precisely tune interlayer twist angle, we plan to measure CT exciton lifetime, emission intensity and behavior with temperature from aligned to misaligned orientation.

We have made a first attempt at fabricating a WSe\textsubscript{2}-MoSe\textsubscript{2} heterostructure device which can be rotated using this method. The bottom half of the device consists of a large MoSe\textsubscript{2}
monolayer on atomically flat bottom BN. The top half is monolayer WSe$_2$ and thin top BN. The halves are fabricated separately and the top half is shaped using photolithography into a circle with protruding facets. We call this shaped WSe$_2$-BN piece the "handle" on which the AFM tip can push. A schematic of the device can be seen in Figure 7.2. Panel (a) shows the top view of the device. The AFM tip (black) is operated in contact mode and moves along the path shown by the yellow arrow. As it moves, the applied force moves the handle of the WSe$_2$-BN top half (grey) along with the tip, causing it to rotate. Panel (b) shows the side view of the device, with the MoSe$_2$ monolayer in red and the WSe$_2$ monolayer in blue.

![Device Schematic](image)

**Figure 7.2: Rotation device schematic (a) top view and (b) side view.**

Our first attempt at using this technique had some initial success. The initial position of the WSe$_2$-BN handle on a large MoSe$_2$-BN substrate can be seen in Figure 7.3(a). When pushed the top half did rotate with respect to the bottom half. However, upon additional pushing, we found the WSe$_2$ detached from the top BN and remained immovable with respect to the MoSe$_2$ monolayer on which it sits. This can be seen in the AFM scan (Figure 7.3b) of the area which showed the handle-shaped WSe$_2$ (region 1) separate from the handle-shaped top BN (region 2).
Additional analysis using low temperature PL and Raman spectroscopy showed WSe$_2$ signature does not appear over the shaped BN handle, region (2), but only in region (1). Additionally, as the handle moves across the surface, residue is pushed in front of it, indicated by the green arrow in Figure 7.3(b). The large amount of surface residue may impede the motion of the handle and indicates cleaner fabrication techniques are still necessary. In addition, after sufficient pushing on the handle, cracks begin to form in the underlying MoSe$_2$. The cracks are indicated in Figure 7.3(b) by red arrows. This may be due to the surface residue building up sufficiently to prevent the handle from rotating further. In this situation, continued force applied to the handle results in force applied to the MoSe$_2$ monolayer in addition to the handle, causing cracks to form.

![Figure 7.3: AFM topographs of the monolayer WSe$_2$-BN handle on a monolayer MoSe$_2$-BN-SiO$_2$ substrate. (a) Initial position of the handle before AFM rotation. (b) Final position of the handle after AFM rotation. Region (1) indicates the location of the delaminated WSe$_2$ monolayer. Region (2) indicates the top BN handle. Buildup of residue is indicated by the green arrow. Cracks in the MoSe$_2$ monolayer are indicated by the red arrows.](image)

We propose using monolayer BN as a lubricant between the MoSe$_2$ and WSe$_2$ monolayers to facilitate rotation. The lattice constants of MoSe$_2$ and WSe$_2$ only differ by 0.1%. Because of this, when commensurate we believe they "lock" to one another as if a single crystal and will take a large force to continue rotation past that point. The same phenomenon does not
occur at the WSe$_2$-BN interface. Therefore, much less force is required to slide WSe$_2$ relative to BN than relative to MoSe$_2$. We believe this is the cause of the WSe$_2$ monolayer delamination. To prevent the WSe$_2$ monolayer from "locking" onto the MoSe$_2$, our next iteration of the device will include a monolayer of BN between the WSe$_2$ and MoSe$_2$ monolayers. Additionally, the new device will be designed to have a bulk area of WSe$_2$ attached to the monolayer WSe$_2$. The AFM tip will then push on the whole WSe$_2$ piece via the bulk material instead of the top BN to prevent the possibility of delamination. With these design modifications, we expect to rotate the top WSe$_2$ precisely with respect to the monolayer MoSe$_2$ on which it sits.
Bibliography