

THERMALIZATION AND EXCITON LOCALIZATION IN 2D SEMICONDUCTORS

by

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DEDICATION

To my parents
Kathleen Strasbourg and Christopher Strasbourg

And to my fiancé
Jessica O'Sell

Thank you for your support.
I could not have done this without you.

In loving memory of
Martha G. Strasbourg

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TABLE OF CONTENTS

1. INTRODUCTION	1
1.1 Layer-Dependent Bandgap of TMD Semiconductors	2
1.2 The Exciton Envelope Approximation.....	8
1.3 Details of the 2D Coulomb Interaction and the Exciton Binding Energy	13
1.4 Introduction to Dark Excitons.....	17
1.5 Overview of Higher Order Exciton Complexes in 1L-WSe ₂	19
1.6 Optical Selection Rules, Valley Magnetism, and Electron-Hole Exchange Interactions: a Topical Introduction	21
1.7 Linear Optical Response of 1L-WSe ₂	25
1.8 Exciton Linewidth.....	29
1.9 Exciton Lifetime	33
1.10 Recoil Broadening of the Luminescence Line Shape for Exciton Complexes.....	35
1.11 Kinetic and Thermodynamic Models.....	37
1.12 Introduction to Quantum Emitters in 2D Semiconductors	40
1.13 Quantum Emitter Formation in 2D Semiconductors	42
1.14 Quantum Emitter Lifetime and Linewidth.....	45
References	46
2. METHODS	59
2.1 Selected Technical Details of the Quantum Optical Microscope	61
2.1.1 Custom Vacuum System for the s50 Cryostat.....	61
2.1.2 Troubleshooting Vacuum Leaks.....	62
2.1.3 Super Continuum Laser Pulse Shape.....	64
2.2 Photoluminescence Excitation Spectroscopy	65
2.2.1 Photoluminescence Quantum Yields in the Presence of Biexcitons	65
2.2.2 Overview of the Photoabsorption Calibration	72
2.2.3 Derivation of the Transfer Matrix Method for Dielectric Thin Films	74
2.2.4 Example Implementation of the Transfer Matrix Method	78
2.2.5 Maintaining a Constant Area of Illumination During the PLE Measurement.....	80
2.2.6 Calibration of the Acousto-Optic Tunable Filter and Active Power Monitoring.....	85
2.3 Time-Correlated Single Photon Counting (TCSPC).....	89
2.3.1 Optics of the Spectrally Resolved TCSPC Apparatus	91
2.3.2 Hanbury-Brown-Twiss Interferometry	93
Chapter 2 References	96

TABLE OF CONTENTS CONTINUED

3. INCREASE OF TRION AND CHARGED BIEXCITON PHOTOLUMINESCENCE QUANTUM YIELDS BY ABOVE-GAP EXCITATION IN SINGLE-LAYER WSe ₂	97
Contribution of Authors and Co-Authors	97
Manuscript Information	99
Abstract	100
Introduction.....	100
Results.....	102
Excitation-Energy-Dependent Linear and Nonlinear Formation of Excitons.....	102
Energy-Dependent Quantum Yields of Trions and Charged Biexcitons	105
Scaling of Enhancement with Excitation Density and the Potential Role of Hot Free Carriers.....	108
Temperature Dependence of the Enhancement Effect.....	112
Discussion	114
Methods.....	117
Sample Fabrication	117
Cryogenic Photoluminescence Spectroscopy	117
Calibration of the Illumination Area for Quantitative Photoluminescence Excitation Spectroscopy	118
Definition of the Excited State Density	119
Linear Photoluminescence Excitation Spectroscopy	119
Reflectance Contrast Spectroscopy.....	119
References.....	126
Supplementary Information: Increase of Trion and Charged Biexciton Photoluminescence Quantum Yields by Above-Gap Excitation in Single- Layer WSe ₂	132
Supplementary Note 1: Saturation Behavior of the Charged Biexciton at Elevated Excitation Densities.....	132
Supplementary Note 2: Transfer Matrix Method Simulations Used to Calibrate the Photoexcitation External Quantum Efficiency.	133
Supplementary Note 3: Discussion of the Low-Energy Resonance in the Excitation spectra.....	135
Supplementary Note 4: Procedure to Estimate the Uncertainty of the Power-Law Fitting.	136
Supplementary Note 5: Estimation of the Quasiparticle Bandgap Energy.	137
Supplementary Note 6: Basic Model of Power-Law Suppression.....	137

TABLE OF CONTENTS CONTINUED

Supplementary Note 7: Additional Evidence for the Optical Generation of Free Carriers by Dual-Color Transient Reflection Spectroscopy.	139
Supplementary Note 8: Trion and Charged Biexciton Power Laws.	143
Supplementary Note 9: Excitation Energy-Dependent Relaxation Dynamics of the Charged Biexciton.	144
Supplementary Note 10: Repeatability of the Enhancement Effect.	145
References.....	146
 4. STRUCTURE-PROPERTY RELATIONSHIPS REVEALED BY SURVEYING THE DYNAMICS OF QUANTUM EMITTERS IN MONOLAYER WSe ₂ SYSTEMS	148
Contribution of Authors and Co-Authors	148
Manuscript Information	150
Abstract	151
Introduction.....	152
Results.....	154
Conclusion	161
References.....	162
Supporting Information for: A Statistical Survey of Excited State Dynamics of Quantum Emitters in Monolayer WSe ₂	174
S1. Materials and Methods	174
Sample Fabrication	174
Optical Measurements	175
S2. Additional Evidence of Quantum Emission	176
1 – Differentiation from Unlocalized Excitons Using Excited State Lifetimes	176
2 – Spatial Localization of the Narrow Emission Lines	176
3 – Evidence for Ubiquitous Emitter Blinking and Spectral Diffusion	177
S3. Additional Room Temperature Photoluminescence Characterization	178
S4. Statistics of the QE Energies	178
S5. Statistics of the QE Linewidths and Deviations from the Transform Limit.....	180
S6. Validation of the Classification of the Kinetics by the Intensity Ratio Metric	181
S7. Additional Discussion of the Metrics used to Classify Excited State Dynamics	181
S8. Rate Model Analysis of Excited State Dynamics	182
1 – Linear Kinetics.....	182

TABLE OF CONTENTS CONTINUED

2 – Nonlinear Kinetics	183
3 – Coupled Sub-Populations.....	184
S9. Additional Cross Sections of the QE Dataset	185
References.....	186
 5. CHARACTERIZATION OF QUANTUM DOT-LIKE EMITTERS IN ARRAYS OF NANOWRINKLES OF 1L-WSe ₂	 197
Contribution of Authors and Co-Authors	197
Manuscript Information	198
Abstract	199
Introduction.....	200
Results.....	202
Discussion.....	210
References.....	211
Supporting Information: Characterization of Quantum Dot-Like Emitters in Arrays of Nanowrinkles of 1L-WSe ₂	 220
Note 1: Using Hilbert Curves to Unpack Hyperspectral Maps.....	220
Note 2: Spatial Distribution of the Doublet Structure in the PL Emission.....	 221
Note 3: Spatial Registration of the AFM Topograph and the PL Intensity Maps.....	 223
 6. CONCLUDING REMARKS.....	 225
6.1 Summary	225
6.2 Future Directions	226
Improvements to the PLE Technique.....	226
Exotic PLE Techniques.....	228
Excitation Spectrum of the Exciton Power Law “Fine” structure	228
Twisted Light PLE	229
Gate Dependence of the Quantum Yield Enhancement effect.....	229
Room Temperature Nano-Optical Activation of 2D QEs	230
6.3 Final Thoughts	232
References.....	232
 CUMULATIVE REFERENCES CITED.....	 235

LIST OF FIGURES

Figure	Page
1. Figure 1.1 – The formation of energy bands in solids.	3
2. Fig. 1.2 – Emergence of the direct bandgap in single-layer transition metal dichalcogenide (TMD) semiconductors upon thinning.	6
3. Figure 1.3 – Schematic of the exciton envelope wavefunction.	12
4. Figure 1.4 – Simulated effects of non-local dielectric screening in a 2D semiconductor.	14
5. Figure 1.5 – Spin-valley configurations of exciton complexes hosted by 1L- WSe ₂ at the K and K' points.	20
6. Figure 1.6 – Bloch and atomic contributions to the orbital angular momentum (OAM) at the K and K' points.	22
7. Figure 1.7 – Trion fine structure. Spin-valley configuration of the intravalley (a) and intervalley (b) trion.	24
8. Figure 1.8 – Example of a dielectric function constructed by superimposing Lorentzian oscillators.	28
9. Figure 1.9 – Temperature dependence of the Exciton linewidth, Γ	31
10. Figure 1.10– Recoil broadening and the formation of a low-energy thermal wing on the PL emission line of an exciton complex (XX).	36
11. Figure 1.11 – Rate model simulations that demonstrate the sensitivity of the charged biexciton saturation density on the doping level.	39
12. Figure 1.12 – Schematic of quantum emitters (QE) in 2D materials.	43
13. Figure 2.1 – Block diagram of the custom laser-scanning confocal microscope used to conduct the experimental work in this thesis.	59
14. Figure 2.2 – Hair on the lid of the cryostat.	63
15. Figure 2.3 – Pulse shape of the supercontinuum laser.	64
16. Figure 2.4 – Energy level diagram showing the branching of an initial population of high-energy excitons (left) or free carriers (right).	68

LIST OF FIGURES CONTINUED

17. Figure 2.5 – Experimental examples that demonstrate the need to maintain a constant excitation density (p_{exc}) to measure the PLQY of biexcitons.	70
18. Figure 2.6 – Cross sectional schematic of a typical hBN/1L-WSe ₂ /hBN sample.	72
19. Figure 2.7 – Comparison of the linear PLE spectrum of 1L-MoS ₂ with and without correction for photonic cavity effects.	74
20. Figure 2.8 – Schematic of the propagating plane waves that are used in the transfer matrix method for dielectric thin films under coherent optical illumination.	75
21. Figure 2.9 – Example photoexcitation external quantum efficiency calculations.	80
22. Figure 2.10 – Simulations of the illumination pattern at the sample when the laser beam is systematically uncollimated.	82
23. Figure 2.11 – Schematic of the computer controlled 2f (Guassian) telescope that was used to prepare the collimation of the laser beam before coupling it into the microscope.	83
24. Figure 2.12 – Experimental setup used to maintain a constant area of illumination during the PLE measurement.	84
25. Figure 2.13 – Schematic of a focused laser spot area and of how the spot area is defined.	85
26. Figure 2.14 – Demonstration of the acousto-optic tunable filter (AOTF) that was used to spectrally filter the supercontinuum laser during the PLE measurements.	86
27. Figure 2.15 – Calibration of the acousto-optic tunable filter.	87
28. Figure 2.16 –Determination of the conversion factor between the power measured at the pickoff position and the power delivered to the sample.	88
29. Figure 2.17 – Operational modes of the HydraHarp400. Left, T2 mode; when the avalanche photodiode (APD) detects a photon, the HH400 logs a detection event relative to global clock. Right, time-resolved emission spectra (TRES) mode.	90

LIST OF FIGURES CONTINUED

30. Figure 2.18 – Selectivity of exit port on the iHR320 spectrometer.	91
31. Figure 2.19– Alignment procedure for the spectrally resolved TCSPC apparatus.	92
32. Figure 2.20- Schematic of the Hanbury-Brown and Twiss (HBT) interferometer.	94
33. Figure 2.21 – Single photon emission from a localized excited state.....	95
34. Figure 2.22 – Experimental signatures of antibunching	95
35. Figure 1 – Enhanced relative emission of trions and charged biexcitons with high-energy photoexcitation and the factors that influence emission intensities of linear and nonlinear states in 2D heterostructures.....	121
36. Figure 2 - Enhancement of the absolute intensity of trions and charged biexcitons with increased excitation energy.....	122
37. Figure 3 – Determination of the energy-dependent quantum yields of the neutral exciton, trion, and charged biexciton in 1L-WSe ₂	123
38. Figure 4 – Power dependence of the quantum yield enhancement and its correlation with exciton formation from free carriers.....	124
39. Figure 5 - Temperature dependence of the quantum yield enhancement of trions and charged biexcitons.....	125
40. Figure S1 – Saturation of the charged biexciton PL emission as measured relative to the PL emission of the neutral exciton.....	133
41. Figure S2 – Calculated photonic cavity resonance of the hBN/1L- WSe ₂ /hBN/SiO ₂ /Si dielectric stack.	134
42. Figure S3 – Dual-color pump-probe transient reflectivity of a 1L- WSe ₂ /hBN sample at room temperature.	140
43. Figure S4 – Excitation spectra of the exciton, inter- and intra-valley trions, and charged biexciton power-law scaling with excitation density.....	143
44. Figure S6 – Excited state relaxation dynamics of the charged biexciton with photoexcitation at 1.98 eV and 2.28 eV.	144

LIST OF FIGURES CONTINUED

45. Figure S5 – Repeatability of the enhancement effect. a photoluminescence acquired while repeatedly cycling the excitation energy between 1.82 and 2.36 eV.	145
46. Figure 1 – Summary of QE samples.	169
47. Figure 2 – Low-temperature photoluminescence (PL).	170
48. Figure 3 – Example photoluminescent transients that demonstrate the variety of kinetics measured.	171
49. Figure 4 – The statistical distribution of effective lifetimes of the emitters measured for each sample.	172
50. Figure 5 – The statistical distribution of intensity ratio, R , which is the ratio of intensity in the second interval of the decay trace to that of the first.	173
51. Figure S2 – Spatially localized photoluminescence from Samples 2 and 3. (a), integrated PL intensity map of the regions under investigation.	187
52. Figure S3 – Spatially localized photoluminescence from Sample 4.	188
53. Figure S4 – Quantum emitter blinking and spectral diffusion.	189
54. Figure S5 – Additional room temperature photoluminescence (PL) characterization.	190
55. Figure S6 – The distribution of energies of the QEs measured.	191
56. Figure S7 – Linewidth analysis of QEs.	192
57. Figure S8 – Characterization of the intensity ratio metric, R . (a) Histogram of R for all PL time transients reported in this work.	193
58. Figure S10 – Additional example photoluminescent transients that demonstrate the variety of kinetics measured.	194
59. Figure S11 – Numerical simulations of excited state dynamics.	195
60. Figure S12 – Corner plots of the effective lifetime, shape metric, linewidth, and energy of each emitter reported in this work.	196
61. Figure 1 – Spatial and spectral inhomogeneity of the 1L-WSe ₂ nanowrinkle array sample.	215

LIST OF FIGURES CONTINUED

62. Figure 2- Variations in the emission intensity and energy of localized excitons.	216
63. Figure 3 – Polarization anisotropy of localized emitters.	217
64. Figure 4 – Time-resolved emission properties and structural correlation of the spectrally isolated emitter.....	218
65. Figure 5 – Sensitivity of the emitters to heating.	219
66. Figure S1 – Comparison of the waterfall plots produced from a hyperspectral PL map by using standard “snake” unpacking versus unpacking the map along a Hilbert curve.	221
67. Figure S2 – Spectral identification of doublets in the PL spectra and their spatial distribution across the sample.	222
68. Figure S3 – Spatial registration of the AFM topograph and the PL intensity maps.	224
69. Figure 6.1 – Proposed experimental setup to measure the dielectric function of 1L-TMD semiconductors that are fully encapsulated in hBN.....	227
70. Figure 6.2 – Material dependence of the enhancement of the charged biexciton.....	229
71. Figure 6.3 – Nano PL of 1L-WSe2 wrinkle array.....	230

ABSTRACT

2D semiconductors are a promising class of materials to investigate for applications in the next generation of photonic devices. They can be used to generate quantum light and also exhibit correlated many-body phenomena. Many of the novel optoelectronic properties of 2D semiconductors are associated with strongly-bound hydrogen-like states known as excitons. Excitons in 2D semiconductors have binding energies on the order of 100s of meV and are stable at room temperature. At low temperatures, higher-order excitonic states such as charged excitons and biexcitons—multiple-bound excitons that are like hydrogen molecules— and localized excitons that emit quantum light are also observed. Whether excited optically or electronically, a diversity of high-energy excitons and free carriers are produced directly after excitation. The relaxation and thermalization of these initial states influence the formation of excitons, biexcitons, and localized excitons. Here, I present work that (i) investigates the thermalization of excited states in a prototypical 2D semiconductor, monolayer (1L-) WSe₂, and reports the discovery that the generation of charged biexcitons is enhanced with increasing photoexcitation energy, (ii) shows the emergence of quantum emitters (QEs) in a new 2D QE platform: 1L-WSe₂ nanowrinkle arrays induced by Au nano stressors, and (iii) uses a novel method to classify the excited-state dynamics of 2D QEs and differentiate emitter populations. A suite of low-temperature energy- and time-resolved optical spectroscopies are used to conduct this work. This work shows how excited state thermalization affects the formation of exciton and biexcitons and investigates the optical properties of an emergent class of 2D quantum light emitters.

CHAPTER 1

INTRODUCTION

2D materials exhibit novel many-body physics in the presence of strong Coulomb interactions. Many 2D materials have a low barrier to entry for experimentation. Remarkably, many of these materials can be isolated using a mechanical exfoliation procedure that essentially only requires bulk crystallites and Scotch tape¹. After exfoliation, monolayers are identified by using basic bright-field optical microscopy and Raman or photoluminescence spectroscopy. Monolayer (1L-) MoS₂^{2,3}, which is a direct bandgap semiconductor within a larger class of layered transition metal dichalcogenide (TMD) materials, was discovered in 2010 using these straightforward fabrication and identification methods. In the years following, more 1L-TMDs were isolated⁴⁻⁹, and a large amount of research effort was focused on fundamental characterization and device integration. 1L-TMD semiconductors are now well established as a valuable class of materials from which a vast amount of nanoscale science has emerged¹⁰⁻²⁰.

The novel characteristics of 2D materials often augment systems in ways that conventional materials cannot. For example, 2D semiconductors exhibit unique phenomena associated with strongly bound excitons and biexcitons²¹⁻²⁵, quantum emission^{26,27}, spin-valley coupling²⁸⁻³², and tunable moiré physics³³⁻³⁶ (when stacked and twisted with other 2D materials) while being readily integrated into devices, possessing extreme strain tunability³⁷⁻³⁹, and being optically and electrically⁴⁰⁻⁴³ addressable. The work here studies thermalization and localization of excitons and biexcitons in 2D materials. Early work on biexcitons in GaAs⁴⁴⁻⁴⁷ and solid-state quantum emitters⁴⁸⁻⁵¹ in other materials provides a foundation on which this work is built.

It is through this lens of emergent physics and device integrability that I present my work here. This work reports (i) the discovery that the generation of charged biexcitons is enhanced with increasing photoexcitation energy beyond the single-particle bandgap, (ii) the emergence of quantum emitters (QEs) in a new 2D QE platform: 1L-WSe₂ nanowrinkle arrays induced by Au nano stressors, and (iii) a novel method to classify the excited-state dynamics of 2D QEs and differentiate emitter populations. In this first chapter, a series of topical introductions to the physics that underpins the journal articles contained in Chapters 3-5 is provided. Then, I introduce select topics that I hope inspire future research. Finally, I include brief statements at the beginning of select sections to contextualize its relationship to this body of work at large.

1.1 Layer-Dependent Bandgap of TMD Semiconductors

When many atoms come into close contact with one another, they can form a solid by bonding with their neighbors. The bonding process involves the redistribution of the valence electrons of the individual atoms across the lattice of the crystal that is formed. These delocalized states form energy bands that dictate the fundamental relationship between the momentum and energy of the electrons in the solid as the electrons traverse the periodic array of atoms, as is shown in Figure 1.1a.

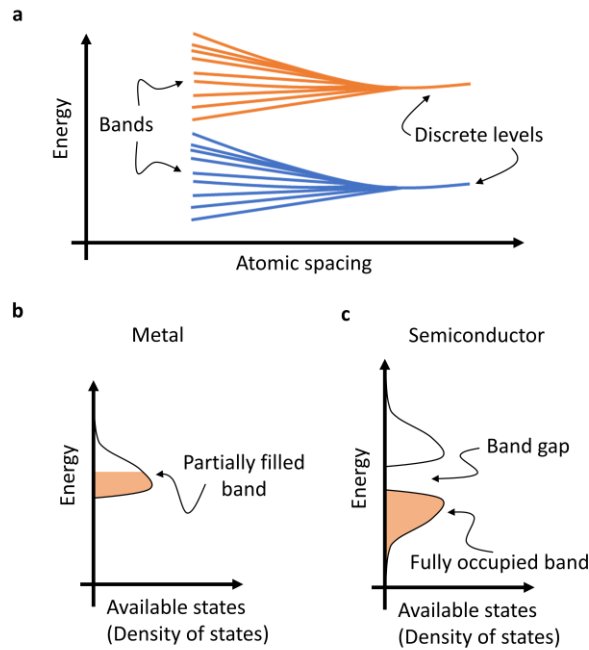


Figure 1.1 – The formation of energy bands in solids. (a) The evolution of the spectrum of many atoms from discrete levels to energy bands as the interatomic spacing is decreased. (b) and (c) Examples of how bands are filled in a semiconductor (c) and a metal (b).

Many of the differences between materials can be captured by how electrons fill these energy bands. Critically, the Pauli exclusion principle dictates that no two electrons—which are fermions—reside in precisely that same state. So, the energy bands are filled up to a point that is determined by satisfying the exclusion principle. For example, metals typically consist of partially filled bands that have empty states residing directly above the occupied states (Figure 1.1b). Consequently, the electrons in metals can respond to external perturbations (e.g., light, electric and magnetic fields, etc.) by readily shifting into the neighboring unoccupied states. This gives metals their high electrical conductivity and characteristic shimmer.

In contrast, semiconductors consist of a filled band that is energetically separated from the next available band of states (Figure 1.1c). In other words, there is a finite energy gap between the bands. The presence of a bandgap is the defining characteristic of a semiconductor. The energy

difference between the bands makes a semiconductor's response to external stimuli significantly different than a metal's due to the energy barrier imposed by the bandgap. Often, the energy needed to overcome the bandgap is provided by light. This process works in reverse, too. Light can be emitted by electrons relaxing back to the lower energy band. The absorption and emission of light at the bandgap encodes information about the structure of the crystal and the interactions that govern the dynamics of electrons that have surmounted the bandgap and can be used in photonic devices for sensing, logic, and energy conversion. The work in this thesis focuses on the interaction between a 2D transition metal dichalcogenide (TMD) semiconductor (1L-WSe₂, in particular) and light.

TMDs are layered semiconductors that consist of stacks of strongly bonded atomic sheets (Figure 1.2a). The atoms within individual sheets are covalently bonded whereas the layers are held together by weaker van der Waals forces. In their bulk form, the extrema of the conduction band and valence band are at different momentum, meaning that the bandgap is indirect. In 1L-TMD semiconductors the band extrema are at the same momentum, i.e., the bandgap is direct. The atomic orbitals that make up the energy bands of the indirect bandgap consist of antibonding p_z orbitals localized on the chalcogen atoms^{2, 3}. The antibonding p_z orbitals extend slightly into the van der Waals gap. So, those electrons can move somewhat easily between the sheets. However, some bands are composed of orbitals localized on the transition metal atoms in the interior of the atomic sheet. Consequently, the electrons in these transition metal d bands are not very mobile between the layers. A useful parameter to characterize the electron mobility between the sheets is the out-of-plane effective mass, $m_{\perp}^*$. The heavier the effective mass, the less mobile the electrons

are between the layers. The d-band states exhibit a significantly greater out-of-plane effective mass than the states composed of the antibonding p_z orbitals.

As the thickness of the TMD crystal is reduced the energy of the indirect bandgap is increased due to the quantum confinement effect⁵². In brief, quantum confinement describes the evolution of the energy spectrum of a nanoscale system as the degree of spatial confinement is increased. The energy shift of the bands in the TMD crystallites due to quantum confinement goes as $\Delta E \sim \frac{\hbar^2}{m_{\perp}^* a^2}$, where $m_{\perp}^*$ is the out-of-plane effective mass and a is the thickness of the crystallite. ΔE only becomes significant in the limit of thin crystallites and for bloch states located at the indirect bandgap due to large $m_{\perp}^*$. The quantum confinement present in a single layer dramatically increases the energy of the indirect gap beyond that of the direct bandgap, as captured by the significant differences in $m_{\perp}^*$.² Figure 1.2 shows how the band gap evolves from indirect to direct as the crystallite is thinned to a single layer.

The transition to a direct bandgap significantly increases the efficiency of light emission. This relationship exists because indirect bandgaps have a momentum mismatch between the extrema of the constituent bands. In contrast, the extrema occur at the same momentum in direct bandgap materials. A direct gap facilitates strong interactions with light whereas indirect bandgaps do not, as explained below.

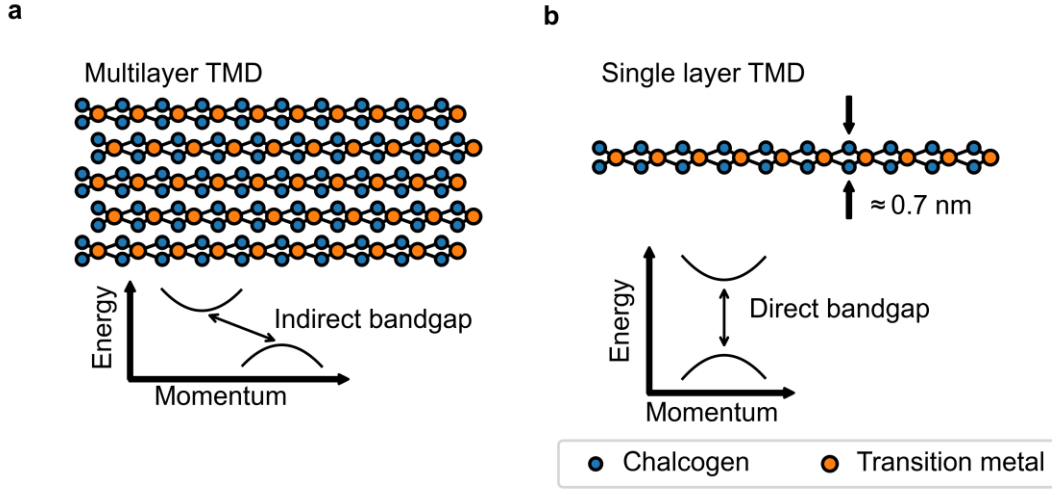


Fig. 1.2 – Emergence of the direct bandgap in single-layer transition metal dichalcogenide (TMD) semiconductors upon thinning. (a) In multilayer crystallites, the edges of the conduction and valence bands are not matched in momentum. (b) In single-layer samples, quantum confinement increases the energy of the indirect bandgap to be greater than the energy of the direct bandgap. So, the single-layer system has a direct bandgap whereas multilayer systems do not. The scatter points are a cross-sectional view of the crystallites.

The large momentum mismatch between the band extrema at indirect bandgaps does not allow electrons to jump across the gap via the absorption or emission of light alone because light carries very little momentum. The momentum carried by light is given by,

$$p = h/\lambda$$

Where h is the Planck constant and λ is the wavelength of light. For light in the visible spectrum (e.g., green light with a wavelength of 532 nm),

$$p_r \approx \frac{6.6 \times 10^{-34} \left[\frac{\text{kg} \times \text{m}^2}{\text{s}} \right]}{532 \times 10^{-9} [\text{m}]} \approx 10^{-27} \left[\frac{\text{kg} \times \text{m}}{\text{s}} \right]$$

In solid-state physics, it is convenient to express the momentum in terms of inverse angstroms by removing a factor of the Planck constant from the momentum. I.e.,

$$\frac{p_Y}{\hbar} = \frac{1}{\lambda} = \frac{1}{5320[\text{\AA}]} \approx 2 \times 10^{-4} [\text{\AA}^{-1}]$$

$\frac{p_Y}{\hbar}$ is insignificant compared to the typical range of momenta spanned by electronic states in a crystal. For example, WSe₂ has a periodicity of 3 Å along its strongly bonded in-plane sheets,

$$\frac{\Delta p_{crystal}}{\hbar} = \frac{2}{3[\text{\AA}]} \approx 1 [\text{\AA}^{-1}]$$

$$\frac{p_Y}{\Delta p_{crystal}} \approx 10^{-4}$$

The momentum that visible light carries is only one part in 10⁴ of the crystal momentum that the electronic states span. Often, indirect bandgaps cover large fractions of the total allowable range of crystal momenta. Photons alone are not able to overcome this momentum mismatch. Thus, light absorption and emission at indirect bandgaps is substantially less likely than at direct bandgaps. In quantum mechanics, the transition probability is well-described by using first-order perturbation theory. Using Fermi's golden rule and the electric dipole approximation, the transition rates are proportional the matrix element,

$$\Gamma \sim |\langle f | r | i \rangle|^2$$

Where $|i\rangle$ is the initial state of the electron, $\langle f|$ is the final state of the electron, and r is the position operator. When there is a large difference in momentum of the initial and final states of the electron the transition rate is suppressed.

Consequently, the transition from an indirect to direct bandgap in 1L-TMD semiconductors is marked by a dramatic increase in the photoluminescence quantum yield (PLQY)^{2,3}. The PLQY is the probability that light is emitted by electrons relaxing back to the ground state after

photoexcitation. This emergent emission enables the identification of single layers by their bright photoluminescence (PL) emission and was reported in the original discovery of 1L-MoS₂^{2, 3}.

Not only does the thinning of the crystallite significantly enhance the PLQY, but the strength of the coulomb interaction between photoexcited charges increases, too. The enhanced Coulomb interaction in single-layer samples leads to the emergence of tightly bound electron-hole pairs, known as excitons. Excitons dominate the optical properties of single-layer TMD semiconductors. Both excitons and the 2D coulomb interaction are discussed at length below.

1.2 The Exciton Envelope Approximation

The exciton envelope approximation quantitatively captures many of the essential properties of electron-hole bound states—excitons—in semiconductors. The exciton envelope approximation is used extensively to connect the non-interacting single-particle picture of Bloch electrons to the few-body dynamics of excitons near band extrema in 2D materials. The approximation is at the necessary level of sophistication to contextualize the physical concepts that constitute this thesis and provides a clear conceptual link between the Bloch picture of non-interacting particles and bound excitons. It is a tremendously convenient framework that is commonly used in both theory and experiment.

Interband transitions in intrinsic semiconductors involve the promotion of a valence band electron into the vacant conduction band of states that reside at higher energy. The collective behavior of the $N - 1$ filled valence states that remain occupied is precisely described by a single positively charged particle that is referred to as a hole. The quantum dynamics of the interacting valence band hole and the conduction band electron are well-described by a Hamiltonian that is like that of a hydrogen atom.

The attractive Coulomb interaction between the two particles manifests a manifold of bound states that are analogous to the solutions of the hydrogen atom, i.e., $\psi = \langle \vec{r} | n, l \rangle$. The principal quantum number, n , describes the radial probability distribution of the electron-hole pair, whereas quantum number l describes the azimuthal rotation of the envelope wavefunction. The envelope function describes the components of an electron-hole wave packet assembled from Bloch states,

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_{s,t} F_{s,t}(\vec{r}_1, \vec{r}_2; n, l) \varphi_{k1,s}(\vec{r}_1) \varphi_{k2,t}(\vec{r}_2)$$

Where the summation is over bands, $k1$ and $k2$ are the crystal momenta, φ are the full Bloch functions, and F is the envelope function whose form is described by the quantum numbers above.

While qualitatively similar, quantitative comparison between excitons in semiconductors and the quantum mechanical model of an isolated hydrogen atom requires nuanced consideration. The first key modification to the hydrogen model is the renormalization of the masses of the constituent particles. In materials, the masses of interacting electrons are renormalized by the many-body Coulomb interactions within the material. This renormalization results in an effective electron mass that can be significantly different than the mass of the free electron. Further, in the hydrogen model, the extreme discrepancy between the masses of the electron and atomic nucleus means that the motion of the atomic nucleus is well approximated as stationary. This simplification is known as the Born-Oppenheimer approximation. Consequently, the eigenstates found in the hydrogen model represent the probability distribution of the electron around the nearly stationary atomic nucleus.

In 2D semiconductors, the interpretation of the wavefunction of the electron-hole system is fundamentally different than that of the hydrogen atom. The effective mass of electrons and holes are comparable. Consequently, the Hamiltonian consists of the position and momentum of two particles⁵³.

$$H(r_e, r_h) = \frac{\vec{p}_e^2}{2m_e} + \frac{\vec{p}_h^2}{2m_h} + \frac{-e^2}{\epsilon_0 \epsilon |r_e - r_h|}$$

The problem is simplified by transforming to the center-of-mass frame,

$$\left(\frac{-\hbar^2}{2\mu} \nabla_r^2 + \frac{-\hbar^2}{2M} \nabla_R^2 + \frac{-e^2}{\epsilon_0 \epsilon r} \right) \psi(r, R) = E \psi(r, R)$$

Disregarding the center-of-mass motion of the electron-hole pair,

$$\left(\frac{-\hbar^2}{2\mu} \nabla_r^2 + \frac{-e^2}{\epsilon_0 \epsilon r} \right) \psi_r(r) = E_r \psi_r(r)$$

The wavefunction of the envelope, $\psi_r(r)$, is representative of the relative separation of the constituent particles and is equivalent to the function, F , above, after transforming to the center-of-mass coordinates. The eigenstates found in this frame should be interpreted as an envelope function that modulates the electron-hole pair density. This framework constitutes the exciton envelope approximation.

The bound state wavefunctions of the exciton envelope approximation correspond to electron and hole configurations that have a well-defined correlation length. For example, the characteristic width of the 1S envelope function, i.e., the exciton ground state, is analogous to the Bohr radius of hydrogen. Excitons with envelopes that extend over multiple unit cells of the underlying crystalline lattice retain much of the characteristics of the Bloch functions that compose the band-edge states. These excitons remain mobile within the crystal and are termed Wannier-

Mott excitons^{54, 55}. In contrast, when the envelope function strongly confines the electron and hole to a region that approaches the size of a single unit cell, the exciton is more accurately described by atomic wavefunctions that are localized on single lattice sites. These excitons are known as Frenkel excitons^{54, 55}. Excitons in 2D semiconductors have a root-mean-square radius of approximately 1.7 nm ⁵⁶ meaning that they are delocalized over approximately 30 unit cells and are reasonably well-described as Wannier-Mott excitons.

Figure 1.3 shows a schematic of the interplay between the localization of the exciton in position space and the spread of the electron and hole wave packets in momentum space. The left panels in Figure 1.3a and Figure 1.3d show a schematic of a delocalized and relatively more localized exciton, respectively. Figure 1.3(b-c) and 1.3(e-f) show the probability distribution of the envelope wave function in position and momentum space, respectively. Generally, the more tightly localized the electron and hole are in position space, the larger the spread of their corresponding wave packets in momentum space.

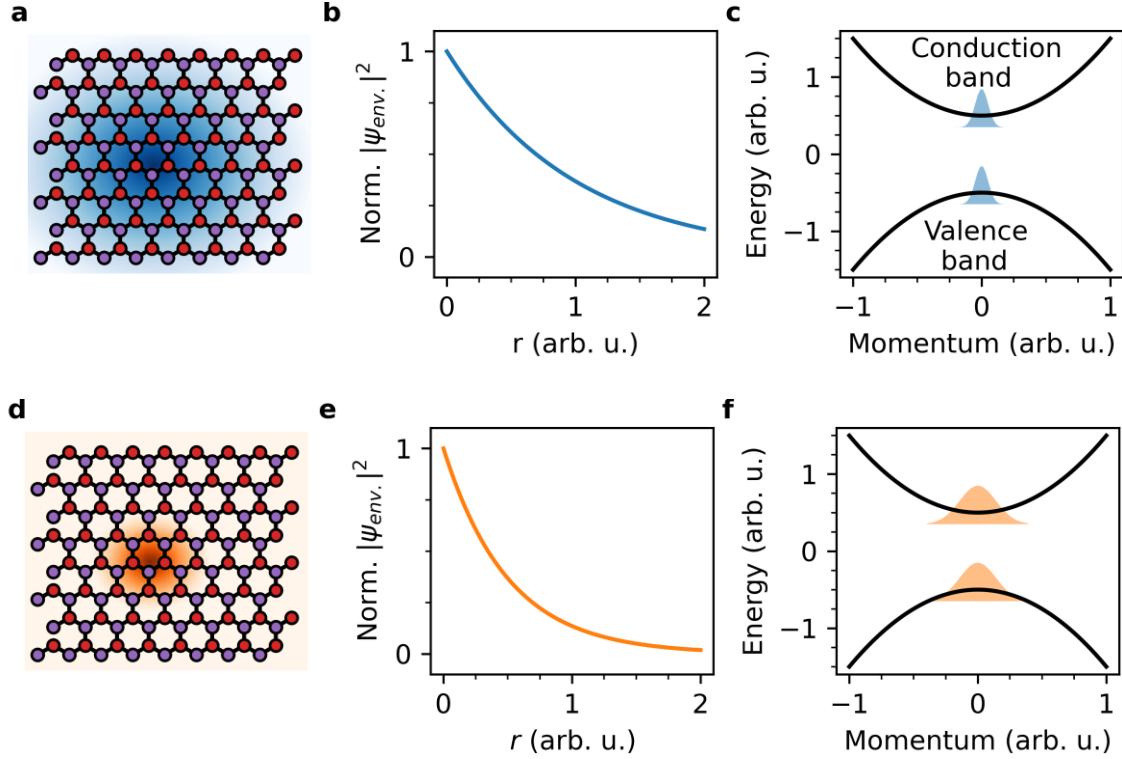


Figure 1.3 – Schematic of the exciton envelope wavefunction. (a) and (d), real space cartoon of the envelope function for a Wannier-mott and Frenkel exciton. The colored shading corresponds to the probability distribution of the electron-hole pair density (i.e., the envelope function) across the crystal lattice (purple and red scatter). (b) and (e), the radial distribution of the envelope wave function in real space. (c) and (f), cartoons of the momentum distribution of the conduction band electron and valence band hole. Confinement in real space induces the spreading of the electron and hole wave packets in momentum space.

As the principal quantum number is increased (e.g., through the exciton Rydberg series), the envelope function becomes more spatially delocalized across the lattice. With sufficient delocalization, the electron-hole bound state is ionized and the 2-particle system is more appropriately described as two non-interacting particles in Bloch states. The interplay between bound and unbound exciton states is essential to the thermodynamics that are considered in this thesis.

1.3 Details of the 2D Coulomb Interaction and the Exciton Binding Energy

The Coulomb force mediates the interaction between charged particles. In 2D materials, the form of the Coulomb interaction is modified due to the reduced dimensionality of the system. Consequently, the spatial distribution and the binding energies of excitons are substantially different than what is found in bulk compounds. The enhancement of the Coulomb interaction underpins a substantial amount of the novel physics investigated in this thesis.

When charged particles are near each other, they exert a mutual Coulombic force on one another. This force is either attractive or repulsive, depending on the sign of the charge on each particle. The interaction is mediated throughout a volume that extends away from the pair. In a vacuum, the finite extent of the interaction volume does not affect the magnitude of the resulting force. However, in real materials, the interaction is screened due to the polarizability of the media that fills the interaction volume. So, for example, the attractive force between an electron-hole pair in a bulk semiconductor is screened by the polarizable semiconductor host material itself. This screening can significantly reduce the strength of the Coulomb interaction and consequently reduce the stability of excitons.

2D materials are significantly more robust against these screening effects. The interaction volume of the Coulomb force extends significantly into the space above and below the plane of the 2D material. Consequently, one of the remarkable advantages of 2D materials over bulk semiconductor counterparts is the ability to engineer the dielectric environment⁵⁷ adjacent to the 2D semiconductor and tune the strength of the Coulomb interaction to enhance excitonic effects.

Rytova and Keldysh first calculated the modification to the Coulomb interaction due to the non-local screening by dielectric layers adjacent to semiconductor thin-films^{58, 59}. More recent

works have utilized a slightly modified formula where the average dielectric constant of the adjacent materials is used^{60, 61}. The Rytova-Keldysh interaction term with non-local screening accounted for is:

$$V(r) = \frac{-e^2}{8\epsilon_0 r_0} \left(H_0\left(\frac{\kappa r}{r_0}\right) - Y_0\left(\frac{\kappa r}{r_0}\right) \right)$$

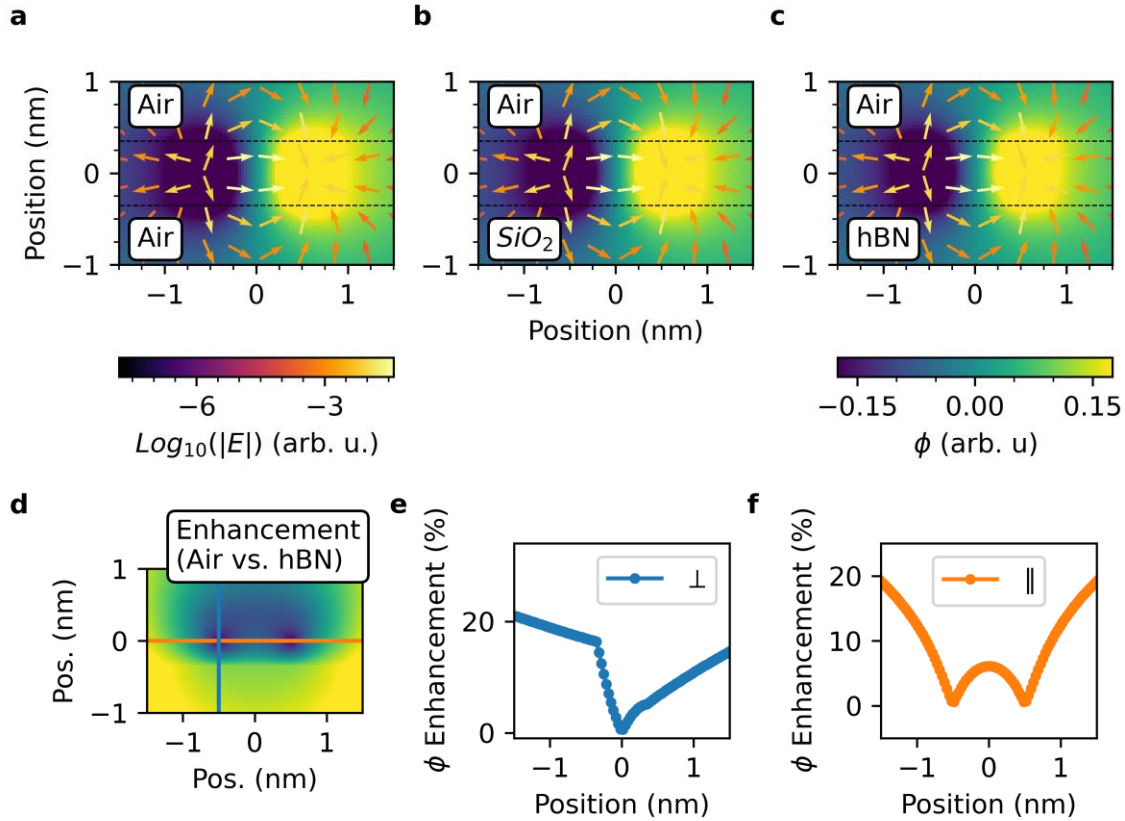


Figure 1.4 – Simulated effects of non-local dielectric screening in a 2D semiconductor. (a-c) Calculations of the electric potential, ϕ , and electric field, E , near an electron-hole pair embedded in a 2D semiconductor and supported by different substrates. Calculations using the method of images for a suspended monolayer (a), SiO₂-supported monolayer (b), and hBN-supported monolayer (c) are shown. (d-f) Enhanced electric potential in the suspended samples versus the hBN support sample. Spatial map of the enhancement (d), a vertical cross of the enhancement section taken perpendicular to the sample stack (e), and a horizontal cross-section through the middle of the 2D material (f).

Where κ is the average dielectric constant of the adjacent layers, r_0 is the characteristic screening length in 2D ($\approx 2\pi\chi_{2D}$) and H_0 and Y_0 are the Struve function and Bessel function of the second kind, respectively. At large interaction lengths, $V(r)$ approaches the typical r^{-1} behavior, while at very small interaction lengths, the potential diverges more slowly as $\text{Log}(r)$. While the Rytova-Keldysh potential is accurate for intermediate charge separations, the logarithmic divergence at small separations is unphysical and limits the applicability of the Rytova-Keldysh model to study the renormalization of the bandgap energy^{62, 63}.

The method of images^{64, 65} provides a slightly more physical model of the static electric potential at all lengths scales. In short, the method of images constructs a solution to the Poisson equation by placing image charges outside of the region of interest to satisfy the appropriate boundary conditions along the dielectric interfaces. Namely, the scalar potential is continuous across each interface and the bound charge accumulated on the interface causes a discontinuity in the gradient of the scalar potential normal to each interface. Figure 1.4a shows the calculated electric potential and electric field lines of an electron and hole separated by 1 nm and embedded in a 2D semiconductor by using a numerical implementation of the method of images up to $N = 201$ image charges. In these simulations, the 2D semiconductor is either suspended ($\epsilon_{\text{top}} = 1$, $\epsilon_{\text{TMD}} \approx 16$, $\epsilon_{\text{bottom}} = 1$), supported by SiO_2 ($\epsilon_{\text{top}} = 1$, $\epsilon_{\text{TMD}} \approx 16$, $\epsilon_{\text{bottom}} \approx 2.25$), or supported by hBN ($\epsilon_{\text{top}} = 1$, $\epsilon_{\text{TMD}} \approx 16$, $\epsilon_{\text{bottom}} \approx 4$). Figure 1.4(d-f) demonstrates that by reducing the dielectric constant of the supporting slab, the strength of the Coulomb interaction is enhanced.

The highest exciton binding energy is realized in systems where the 2D material is suspended in free space. This configuration can be achieved, for example, by suspending the sheet over micro cavities⁶⁶. Suspended monolayers benefit from negligible screening by the surrounding

media and host excitons with binding energies on the order of 500-800 meV⁶⁷⁻⁶⁹ but suffer from inhomogeneous strain fields imparted to the 2D material and other unattractive qualities introduced during sample fabrication.

2D semiconductors that are directly exfoliated onto silicon substrates are substantially simpler to produce than suspended samples while retaining strong Coulomb interactions. The screening by the supporting SiO₂ layer is minimal ($\epsilon_{\text{SiO}_2} \approx 2$) and the exciton binding energy is only slightly weakened to ~350-450 meV. Yet, interfacial disorder along the SiO₂ and 2D material interface can significantly degrade the pristine optoelectronic properties of the 2D semiconductor^{65, 70-72}. Finally, encapsulation in hBN^{61, 72, 73}—a layered wide bandgap material—significantly enhances the optoelectronic properties of 2D semiconductors by drastically reducing the interfacial disorder associated with traditional substrates. While hBN has a relatively large dielectric constant (≈ 4.5) as compared to silica, the additional screening only reduces the exciton binding energy to approximately 200 meV when the top capping layer of hBN is thin⁶¹.

Even when encapsulated in hBN, exciton and biexciton physics are prevalent at low temperatures. Encapsulation in hBN also has the added benefit of enhancing optoelectronic properties by significantly reducing carrier scattering and non-radiative recombination due to interfacial disorder. Finally, as a point of comparison, the exciton binding energy in GaAs quantum wells is approximately 10 meV⁴⁷, significantly lower than the binding energies of excitons in 2D materials.

1.4 Introduction to Dark Excitons

The coupling between excitons and light strongly depends on the alignment of the spins of the constituent electron and hole. A fine structure of bright- and dark-excitons arises from the spin-splitting in the conduction and valence bands of 1L-TMD semiconductors. In 1L-WSe₂, the dark exciton is the lowest energy exciton. Consequently, the dynamics of the dark exciton population are imprinted on the spectroscopic experiments that I discuss throughout this work. Dark excitons are inextricably linked to processes that are of utmost importance in this work. Here I introduce them.

Wanier-Mott excitons retain much of the Bloch character of the band-edge states of which they are composed. As the strength of the Coulomb interaction between carriers is increased, a manifold of Rydberg-like bound states emerges within the single-particle bandgap of the semiconductor. The emergence of these states as the interaction strength is increased demonstrates how the non-interacting single-particle system evolves into the interacting electron-hole system. Consequently, the electronic structure that exists within the bands of the underlying semiconductor will approximately be retained by the excitonic bound states in the interacting 2-particle system.

In 2D TMD semiconductors, strong spin-orbit splitting in the valence band and relatively weaker spin-orbit splitting in the conduction band at the K-point have a profound effect on the coupling of excitons to light. The Bloch states in the valence band at the K-point consists primarily of the transition metal $d_{x^2-y^2}$ and d_{xy} orbitals, which manifest strong spin splitting in the valence band. In the conduction band, first-order contributions by the chalcogen p_x and p_y orbitals along with second-order contributions from the d_{xz} and d_{yz} orbitals weakly split the band¹⁴. The energetic ordering of the spin-polarized branches of the conduction band is determined by the

interplay between the contributions to the splitting by the transition metal d orbital and the chalcogen p orbitals. For example, in molybdenum-based TMDs (e.g., MoS₂ and MoSe₂), the ground state exciton consists of a spin anti-aligned electron-hole pair, yet in tungsten-based TMDs (e.g., WS₂ and WSe₂) the energetic ordering of the spin-polarized conduction band is reversed and the ground state exciton consists of a spin aligned electron-hole pair (where spin projections for holes in a given band are opposite of that of electrons). These excitons are commonly referred to as the spin-singlet and spin-triplet excitons, in analogy to a basic two-electron system. Due to the aligned spins of the exciton triplet, radiative recombination is prohibited due to the inability of optical dipoles (i.e., interaction with light) to flip the spin of a constituent particle, since there is not a term that couples the electronic spin to light in the light-matter Hamiltonian. E.g., the electromagnetic vector potential is including in the Hamiltonian by transforming the momentum operator, $\vec{p}$, to include the vector potential, $\vec{A}$,

$$\vec{p} \rightarrow \vec{p} + \vec{A}$$

Which does not directly couple light to the spin degrees of freedom of the electron.

Consequently, the exciton triplet is termed the “spin dark” or, more simply, “dark” exciton⁷⁴⁻⁷⁷, and the exciton singlet is termed the “bright” exciton. The dark exciton has a dramatically enhanced lifetime (≈ 100 ps in WS₂ at 4 K⁷⁸) compared to the bright exciton (< 2 ps in MoS₂ at $T = 4$ K), increasing the scattering probability with additional carriers and other excitons, which enhances the formation of higher order bound states (e.g., biexcitons) in W- based TMDs.

1.5 Overview of Higher Order Exciton Complexes in 1L-WSe₂

The strong Coulomb interaction in 2D TMDs stabilizes states that consist of multiple electron-hole pairs. In this thesis, I report the discovery that the generation of some of these complexes is enhanced by photoexciting with energy beyond the single particle bandgap.

The strong Coulomb interaction in 2D semiconductors also stabilizes higher-order excitonic states composed of 3, 4, and 5 quasiparticles. The spin-valley configuration of these states is shown in Figure 1.5. The exciton consists of a spin-aligned electron-hole pair while the spin-dark exciton consists of a spin-opposed electron-hole pair (here, spin projections are labeled by the electron's spin state). There are two valley configurations of the charged exciton (called "trions"); the inter-valley trion and the intra-valley trion. There are two species of bound states that consist of two excitons (called "biexcitons"); the neutral and charged biexciton.

The binding of an additional electron or hole to the neutral exciton complex forms a three-particle charged exciton species known as the trion⁷⁹⁻⁸¹. In lightly n-doped WSe₂, the negatively charged trion is observed as a low-energy PL emission feature. Trions are particularly appealing for enhancing exciton transport, realizing Stark-tunable PL emission energy, and electrostatic gating of PL emission intensity^{79, 81}. Trions typically have a binding energy of approximately 20 meV and begin to stabilize below 200 K.

The neutral biexciton^{21, 40, 82, 83} also emerges at sufficient excitation densities and low temperatures. Biexcitons are analogous to the hydrogen molecule and result from the binding of two neutral excitons. Biexcitons are particularly appealing for applications that seek to leverage their nonlinear formation, unique valley properties⁸², and potential for entangle photon pair generation via a cascaded emission process when localized⁸⁴.

Finally, in 1L-WSe₂ samples that are fully encapsulated in hBN and at low temperatures, charged biexciton states have also been observed^{22, 23, 25, 85}. The charged biexciton consists of a coulombically bound trion and exciton. These 5-particle complexes retain much of the appealing properties of the neutral biexciton complex while adding a wider range of gate- and Stark-tunability due to the net charge that is acquired. Neutral and charged biexcitons exhibit binding energies of approximately 15 meV and begin to stabilize below 175 K, with resolvable PL emission below approximately 80 K.

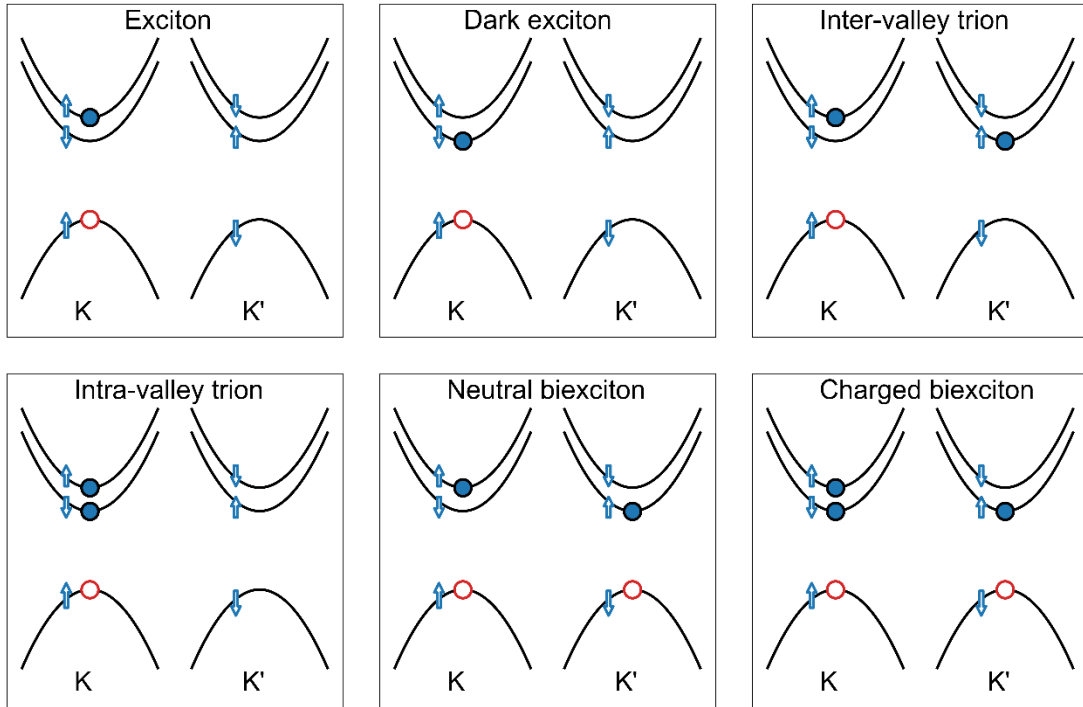


Figure 1.5 – Spin-valley configurations of exciton complexes hosted by 1L-WSe₂ at the K and K' points. The electron spin states of the bands are labeled by the blue arrows. Red and blue scatter points denote valence band holes and conduction band electrons, respectively. The conjugate valley configurations for each complex are not shown. The lower spin-split valence band is excluded from these diagrams.

While trions are readily observed in both Mo- and W- based 1L-TMDs, the biexciton complexes are substantially more prevalent in W- based 1L-TMDs such as 1L-WSe₂. This exemplifies the interplay between the lifetime of the ground state exciton and the formation of the higher-order complexes. At dilute exciton densities, the formation of the biexcitons will sensitively depend on the probability that the two constituent species become sufficiently close to one other to coulombically bind. The probability of the interaction is proportional to the lifetimes of the constituent states, making biexciton formation in Mo-based TMDs substantially less efficient than in W-based TMDs.

1.6 Optical Selection Rules, Valley Magnetism, and Electron-Hole Exchange Interactions: a Topical Introduction

The honeycomb crystal lattice and spin polarization at the band-edges of the direct bandgap in 1L-TMDs lead to several astounding properties. For example, spin-valley locking couples the spin and valley degrees of freedom which leads to chiral selection rules. Strong Coulomb exchange interactions lead to the emergence of massive Dirac physics and pronounced exciton and trion fine structure. While not immediately relevant to the research presented in this thesis, these effects set the basis for more in-depth follow-up studies on the evolution of the quantum dynamics of valley excitons and biexcitons and also lay the groundwork to interpret magneto-optical data. Here, I topically introduce some particularly interesting concepts that may inspire additional work.

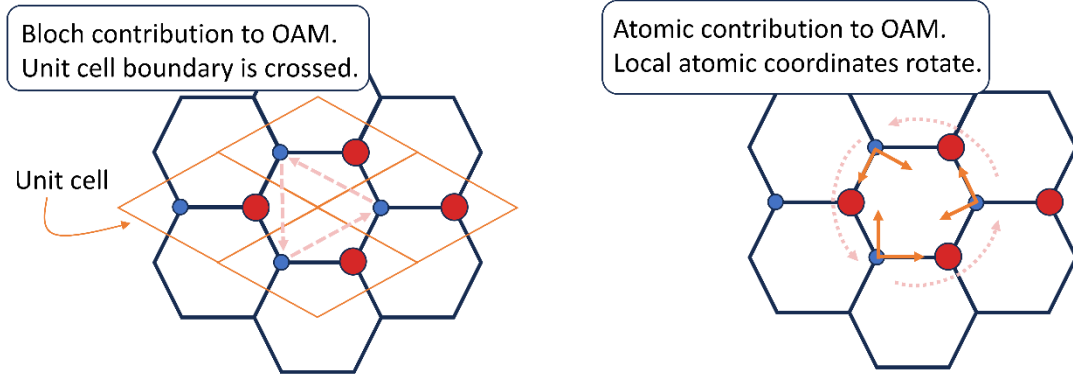


Figure 1.6 – Bloch and atomic contributions to the orbital angular momentum (OAM) at the K and K' points. Left, the Bloch contribution to the phase winding under three-fold rotation. Each rotation maps the wavefunction across the boundary of the unit cell. Right, the atomic contribution. The local atomic coordinates are rotated, which winds the phase of the Wannier functions.

The chiral selection rules at the bandgap are a fundamental optical property of 1L-TMD semiconductors. In TMD monolayers, there are two degenerate valleys at the corners of the hexagonal Brillouin zone where the direct bandgap resides (K and K'). The low-energy physics at the bandgap is captured by a 3-band model^{14, 31} that consists of a spin-polarized valence band and two spin-polarized conduction bands. The valence band consists of the states composed of the transition metal $d_{x^2-y^2}$ and d_{xy} orbitals (i.e., $|l, m\rangle = |2, 2\rangle$ and $|2, -2\rangle$ at K and K') while both conduction bands consist of transition metal d_{z^2} orbitals (i.e., $|l, m\rangle = |2, 0\rangle$). Following the discussion in⁸⁶, the total magnetic quantum number, m , is determined by phase winding of the wavefunction under 3-fold rotation. Competition between the atomic and Bloch functions emerges due to the symmetry of the honeycomb lattice. Figure 1.6 illustrates these two contributions to the orbital angular momentum at the K and K' points. The atomic contribution is determined by sampling the winding of the $l = \pm 2, 0$ atomic orbitals under the 3-fold rotation, resulting in a net contribution of $\mp 1, 0$. On the other hand, the rotation also causes the wavefunction to pick up an

additional phase due to crossing the boundary of the unit cell. This can be seen by recognizing that a 3-fold rotation maps the periodic part of the Bloch wavefunctions into a neighboring unit cell. The phase factor is then given by the Bloch theorem,

$$\psi(\vec{r} + \vec{a}) = e^{i\vec{k} \cdot \vec{a}} \psi(\vec{r})$$

Where $\vec{k}$ is the crystal momentum and $\vec{a}$ is a lattice vector into the neighboring unit cell. The net result is that the total orbital angular momentum at the valence band edge is $m = 0$ whereas at the conduction band edge $m = \pm 1$, where the sign of the magnetic quantum number is determined by the valley. Therefore, the conservation of orbital angular momentum dictates that an optical transition at K (K') results in the absorption or emission of circularly polarized light, with chirality dictated by the valley index (K or K').

In the presence of a magnetic field, the shift of the bright exciton resonance is captured by the effective spectroscopic g-factor, g_{eff} . g_{eff} depends on the relative shift of the energy of the conduction and valence bands. Spin is conserved in optical transitions, and consequently does not contribute to g_{eff} . In contrast, the atomic orbital angular momentum of the bands contributes substantially due to the difference between the atomic orbital contribution in the conduction band ($m = 0$) and valence band ($m = \pm 2$). The valley orbital angular momentum also contributes to g_{eff} with a contribution of $\pm \approx 1$ ^{87, 88, 89 32, 87, 89}.

Furthermore, the strong Coulomb exchange interaction in TMDs^{90, 91} mixes the bright excitons at the K and K' points with finite center-of-mass (COM) momentum. This mixing strongly modifies the exciton dispersion into gapless Dirac bands consisting of hybridized valley excitons^{87, 90, 92}. The mixing of the valley states takes place with a coherence time that can be measured with a relatively simple PL experiment where the depolarization time of the linear polarization

anisotropy is measured after excitation⁹³⁻⁹⁵ (termed a valley coherence measurement). A future study might investigate the excitation energy spectrum of the valley coherence time to unveil the roles of excited state relaxation and thermalization in the formation (destruction) of valley superposition states. This has not been reported yet, to my knowledge.

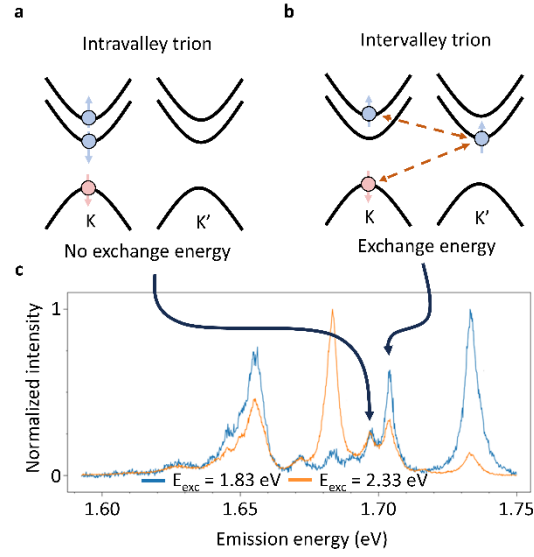


Figure 1.7 – Trion fine structure. Spin-valley configuration of the intravalley (a) and intervalley (b) trion. There is an exchange energy (orange arrows) associated with the electron-electron and electron-hole interactions in the intervalley trion. (c) An example PL spectra of 1L-WSe2 at 4 K. The trion fine structure splitting is observed in the PL.

The strong Coulomb exchange interaction also opens a gap in the trion dispersion^{87,90}. The gap distinguishes the configurations of the trion that hosts the additional electron in the same valley as the exciton (i.e., the intra-valley trion) versus the conjugate valley (i.e., the inter-valley trion). The exchange interaction stabilizes the gap without an external field, which makes the relatively higher energy optical resonance associated with the inter-valley trions resolvable in low-temperature optical measurements^{96,97}. Figure 1.7 shows the spin-valley configurations of the trion fine structure and presents a typical 4 K PL where the splitting is observed.

1.7 Linear Optical Response of 1L-WSe₂

Beyond the lowest energy excitons at the K-point, there are higher energy excitons and interband transitions that contribute significantly to the optical properties of 1L-TMDs across the visible spectrum of light. Modeling the optical absorption of these higher energy resonances was critical in conducting the quantitative excitation spectroscopy presented in a later chapter. Here, I give a summary of the origin of these resonances and briefly discuss challenges associated with modeling the dielectric function of 1L-WSe₂.

While the luminescence spectrum of 1L-TMDs is rich with emission from both single- and higher-order exciton states, the higher-order exciton complexes tend to contribute very weakly to the direct absorption of light under typical excitation conditions. There is, however, strong light absorption spanning the visible spectrum that is mediated by the bright exciton states at the K-point⁹⁸, higher energy excitons^{99, 100}, and additional interband transitions in the so-called exciton continuum^{100, 101}.

Here, it is useful to summarize additional terminology to describe these states. The lowest energy bright exciton hosted at the direct gap in 1L-TMDs is termed the “A” exciton^{2, 3}. Often, it is relevant to also include the principle quantum number of the exciton envelope wave function to distinguish light absorption by the Rydberg excitons within a given exciton manifold. For example, “A_{1S}” denotes the bright ground state exciton, whereas “A_{2S}” is the next excited state and denotes the slightly more delocalized Rydberg A exciton wave function. Typically, light absorption by the A_{1S} exciton in fully encapsulated 1L-WSe₂ at low temperature occurs at approximately 1.74 eV (712 nm), whereas light absorption from the A_{2S} exciton occurs at 1.87 eV (663 nm).

Approximately 400-500 meV higher in energy than the A_{1S} exciton absorption resonance is the B_{1S} resonance. The B exciton corresponds to the K-point exciton whose hole is hosted in the lower spin-split conduction band. The energy separation between the A_{1S} and B_{1S} resonances is predominantly reflective of the spin-orbit splitting in the valence band at the K-point. Energetically between the A and B exciton absorption resonance lies the quasiparticle bandgap (QPBG). The QPBG corresponds to the minimum energy needed to generate unbound electron-hole pairs (i.e., Bloch particles) in the continuum of the A Exciton. Typically, the QPBG is unobservable using standard optical spectroscopy techniques in materials with strong excitonic resonances. The otherwise sharp QPBG absorption resonance is softened into a continuum that merges with the A exciton Rydberg states due to the transfer of significant oscillator strength to the exciton absorption resonances^{99, 102}. In fully encapsulated 1L-WSe₂, the QPBG energy is estimated to be approximately 2.0 eV (620 nm)⁶¹.

Above the QPBG, optical absorption is resonant with high-energy excitons, continuum transitions, or both. Beyond the QPBG and the A and B exciton manifolds, light absorption near the high-energy edge of the visible spectrum is mediated by the C absorption resonance at approximately 2.55 eV (486 nm)^{67, 103}. The origin of the C resonance is thought to be either the ground state of a high energy exciton located at the Γ -point¹⁰⁴ (zone center) in the Brillouin zone or due to the nesting of the valence and conduction bands away from the band extrema at the crystallographic high-symmetry points^{103, 105}. Band-nesting, in short, describes a region in momentum space where two bands run parallel to one another. This feature in the band structure substantially enhances the joint density of states at the energy that the bands are offset from one another and commensurately increases the strength of the corresponding interband optical

transition¹⁰⁵. Regardless of the microscopic origin of the C resonance, 1L-WSe₂ absorbs light from approximately 1.74 eV to significantly greater than 2.55 eV by both exciton and continuum resonances.

The light-matter interactions described above are phenomenologically described by the material-specific optical response function. To capture the response of 1L-WSe₂ under moderate illumination intensities, it is appropriate to only consider the linear optical response of the semiconductor¹⁰⁶. This significantly reduces the complexity required to model the dielectric function by enabling the use of linear response theory.

One of the key considerations when modeling the dielectric response is satisfying the Kramers-Kronig relationships which ensure a causal response of the material under interrogation. In short, the Kramers-Kronig relationship stems from the constraint that an optically induced polarization in the material cannot precede the illumination itself. Since the dielectric function is a response function in the frequency domain (i.e., is a function of the energy of the incident light), causality is enforced by integral equations that precisely define the relationship between the real and imaginary parts of the dielectric function⁵⁴.

Satisfying causality limits the functional forms that the dielectric function can adopt. Generally, most functions in the complex plane do not satisfy the Kramers-Kronig condition. Thus, to model the dielectric response of real materials where complete ellipsometric characterization may be infeasible, it is useful to consider the superposition of functions that individually satisfy causality. One such function is the complex Lorentzian, which has physical origins in the response of an electron moving in the presence of an oscillating electric field. By using a superposition of so-called Lorentzian oscillators, the optical response of many 2D semiconductors on Si/SiO₂

substrates has been successfully extracted from analysis of basic normal incidence white-light reflectance spectra and subsequent constrained Kramers-Kronig analysis using a series of superimposed Lorentzian oscillators^{79, 107}.

An example of a dielectric function constructed by the superposition of Lorentzian oscillators is shown in Figure 1.8. In this schematic, six oscillators are superimposed to construct a dielectric response function that mimics the real response of 1L-WSe₂. While the example shown in Figure 1.8 is for demonstration, the parameters of each oscillator (oscillator strength, linewidth, position, etc.) can be varied to fit spectroscopic data that is experimentally measured, as is done commonly in literature^{79, 107}.

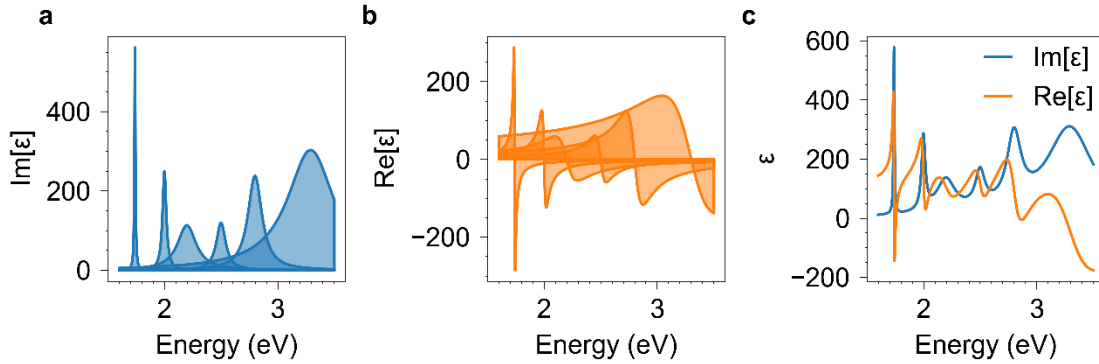


Figure 1.8 – Example of a dielectric function constructed by superimposing Lorentzian oscillators. (a) The imaginary components of the individual oscillators. (b) The real components of the individual oscillators. (c) The full complex response function is constructed by superposition. The imaginary and real components of ϵ are shown in blue and orange, respectively.

While the dielectric functions found in materials supported by standard Silicon wafers are qualitatively like the dielectric response of materials encapsulated by hBN, the precise oscillator strengths, linewidths, and transition energies of the resonances will be slightly different in hBN-supported versus silica-supported monolayers. Yet, modeling a reflectance spectrum of a 2D

material heterostructure presents a significant technical challenge: photonic cavity effects stemming from interference within the stratified stack of dielectric materials (e.g., hBN/1L-WSe₂/hBN/SiO₂/Si).

1.8 Exciton Linewidth

The linewidths of optical resonances encode information about the lifetimes, coherence times, and disorder landscape of the system under investigation. Additionally, the linewidth can reveal information about the thermalization of many-body states. In a later chapter, we present statistical characterizations of the linewidths and excited state lifetimes of quantum emitters hosted in a variety of 1L-WSe₂ systems and estimate the degree to which random fluctuations broadens the emission line. Here I summarize some of the factors that determine the optical linewidths of excitons in 2D materials.

Excitons in 2D materials have relatively short coherence times due to their large oscillator strengths, strong electron-phonon interaction, and substantial dephasing due to scattering with other excitons. Temperature-dependent studies have investigated the exciton linewidth by successfully employing a simple phenomenological model to capture the predominate radiative and nonradiative contribution to the PL linewidth of the ground state A exciton. In this model, there are three contributions to the homogeneous linewidth^{108, 109}:

$$\Gamma = \Gamma_0 + aT + \frac{b}{e^{\Delta/k_bT} - 1}$$

The zero-temperature linewidth, Γ_0 , is well approximated by radiative linewidth in high-quality materials and is proportional to the overlap of the electron-hole wavefunctions. The second term captures dephasing due to the enhanced interaction with acoustic phonons at elevated

temperatures, and the third term describes dephasing due to the interaction with optical phonons. The third term includes a Bose factor to capture the temperature dependence of the thermal phonon population. By measuring the temperature dependence of the exciton emission linewidth, the relative strengths of the phonon broadening mechanisms and the intrinsic linewidth can be deduced. It is worth noting, though, that extracting the homogenous linewidth from luminescence data can be complicated by inhomogeneous broadening⁷² (discussed below), shallow trap states (i.e., Urbach tails⁵⁴) and the emergence of additional exciton complexes at sufficiently low temperatures.

Figure 1.9 shows an example of how the linewidth of the exciton narrows upon cooling in a high-quality 1L-WSe₂ sample that is fully encapsulated in hBN. From the experimental data, the temperature dependence of the FWHM is extracted and fitted with the model described above. A zero-temperature linewidth of 6.2 meV is found and an optical phonon activation energy of 46 meV is inferred by the fit, which is in good agreement with the energies of optical phonons reported in the literature.

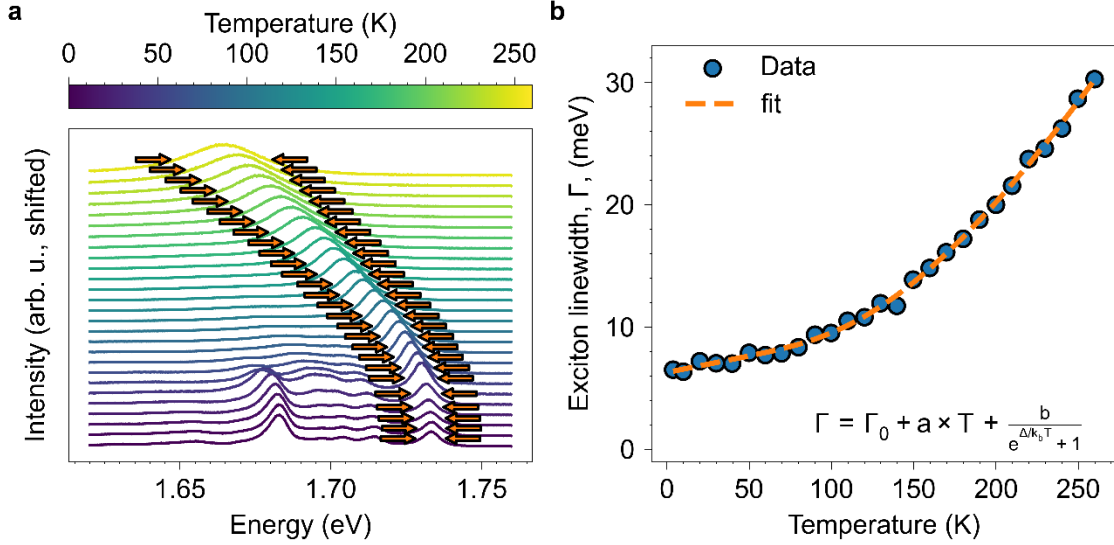


Figure 1.9 – Temperature dependence of the Exciton linewidth, Γ . (a) Temperature-dependent photoluminescence of 1L-WSe₂ fully encapsulated in hBN ($E_{\text{exc}} \approx 2.1$ eV and $p_{\text{exc}} \approx 1011$ cm⁻²). The full width at half maximum of the Exciton PL emission line is indicated by the opposing arrows. (b) The temperature dependence of the Exciton linewidth. The linewidth is shown in the blue scatter and a fit using the objective function that is annotated is shown in orange. Best fit parameters; $\Gamma_0 \approx 6.2$ meV, $a \approx 26$ $\mu\text{eV/K}$, $b \approx 117$ meV, $\Delta \approx 46$ meV.

Exciton-exciton interactions also dephase the exciton population, resulting in the emergence of an additional broadening mechanism at large excitation densities. The exciton-induced-dephasing rate scales linearly with the exciton density and was characterized in studies that leveraged four-wave-mixing experiments¹¹⁰.

The homogeneous linewidth is intimately related to the coherence time of the excitons. Despite achieving ultra-high-quality samples via self-flux-based growth techniques and hBN encapsulation, the coherence time is limited by the fast relaxation rates of tightly bound excitons in 2D materials. Typical coherence times of the ground state exciton are on the order of hundreds of femtoseconds to single picoseconds¹¹⁰, depending on the energetic ordering of the bright-dark exciton fine structure and lattice temperature. This short coherence time is a fundamental challenge for the utilization of delocalized excitons in 2D semiconductors in quantum technologies that rely

on emitters or qubits that need to be controlled with gate operations. But, as discussed in a later chapter, localized excitons in 2D semiconductors exhibit significantly longer lifetimes, emit single photons, retain many of the appealing band-edge properties unique to 2D semiconductors, and can be placed with nanoscale precision, making them appealing candidates for the production of quantum light.

Typical values for the homogeneous linewidth of excitons range from 2 – 10 meV, depending on material quality and the degree of interfacial disorder. As mentioned above, encapsulation in hBN dramatically reduces interfacial disorder as compared to standard supporting Silica substrates. The narrowest linewidths have been achieved in samples fully encapsulated in hBN.

Regardless, homogeneous linewidths of delocalized excitons in 2D materials are rarely directly observed in linear optical spectroscopy experiments due to the prevalence of inhomogeneous broadening. When using far-field optical characterization methods, the spatial resolution is at best diffraction-limited, meaning that the minimum area that the measurement probes is on the order of the wavelength of light (typically 400 – 800 nm, depending on the numerical aperture of the microscope objective). Regions of this size can include significant nanoscale inhomogeneity, which broadens the distribution of transition energies of the homogeneous resonance over the finite extent of the measurement area. For example, nanoscale disorder in the local dielectric environment¹¹¹, charge puddling¹⁰², and variations in the atomic spacing (i.e., strain) are pervasive in samples that do not employ careful fabrication techniques to limit their effects. The disorder landscape can be well-described by a normal distribution (i.e., Gaussian) and manifests as a broadened optical line shape that is accurately modeled as a

convolution of the homogenous—Lorentzian—line and the inhomogeneous—Gaussian—line (i.e., the inhomogeneously broadened line is a Voigt function). Inhomogeneous broadening can substantially mask the homogenous linewidth of oscillators, limiting the information that can be inferred about scattering channels and dephasing mechanisms from the measured optical linewidths.

1.9 Exciton Lifetime

After optical or electrical excitation, the exciton population begins to relax back to the semiconductor ground state. These dynamics are described by the lifetime of the exciton species. The lifetime of an exciton population can lend insight into the scattering processes that define key emitter metrics such as coherence times, population lifetimes, brightness, and formation and relaxation pathways. In each of the journal articles contained in later chapters, measurements of the excited-state lifetime are used to extract critical information about the exciton population dynamics. For example, lifetime measurements are used to show that the enhancement of the charged biexciton quantum yield at elevated excitation energies is not due to an increase in the efficiency of its radiative decay, that Auger processes can dominate the dynamics of certain classes of quantum emitter (QE) platforms, and that the decay dynamics of a strain-localized QE is consistent with previous reports. Here I introduce the concept of emitter lifetime.

In the simplest form, the lifetime of an exciton population can be modeled as the exponential decay of the population,

$$\frac{dN(t)}{dt} = -\tau^{-1}N(t)$$

Where τ is the lifetime of the population and N is the number of excitons. In later chapters, we implement more complex rate models that capture the effects of nonlinear processes such as Auger recombination and biexciton formation, but the simple model described here is sufficient for comparisons between populations that exhibit sufficiently linear dynamics. In the following, I discuss the underlying physical processes that contribute to the value of the lifetime, τ .

Auger scattering, a process in which an exciton non-radiatively recombines by transferring its energy to a Bloch electron via a Coulomb interaction, can accelerate the recombination kinetics of excitons in 2D semiconductors. More generally, Auger-type processes can occur between carriers, excitons and carriers, multiple excitons, etc. The strength of an Auger process depends sensitively on the pair density of the reactants and the strength of the Coulomb interaction. At elevated excitation densities in 2D materials, Auger scattering can dominate the excited state population dynamics. Furthermore, the charge capture rate by defects in 2D semiconductors is substantially enhanced by Auger-assisted processes that are as ubiquitous as excitons themselves¹¹². Consequently, Auger processes have a profound impact on the formation of quantum emitters, the PLQY of excitons, and the population lifetimes of excited states in 2D semiconductors. Additional details are discussed in later chapters.

The momentum distribution of excitons also affects the lifetime. Even at liquid helium temperatures, a thermalized exciton population has a relatively large width in momentum space. Consequently, momentum conservation prohibits the radiative recombination of excitons with sufficiently large center-of-mass momentum because of the small linear momentum carried by photons. The maximum momentum that a photon can carry at a given energy (i.e., the radiative light cone) defines the fraction of the thermalized exciton population that can radiatively

recombine. Thus, the effective radiative recombination rate for a thermal distribution of excitons is typically much slower than the intrinsic radiative lifetime.

Resonantly exciting excitons can drastically accelerate the effective radiative rate toward values that approach the intrinsic recombination time¹¹³. Resonant excitation initializes a nonthermal distribution within the light cone. This non-thermal distribution possesses a characteristic thermalization time that strongly depends on the lattice temperature. Consequently, at low temperatures the thermalization time can be on the order of the intrinsic radiative rate, meaning that a significant portion of the initial nonthermal exciton population can be rapidly depleted via radiative recombination before the population thermalizes.

1.10 Recoil Broadening of the Luminescence Line Shape for Exciton Complexes

Conservation of momentum requires that optical transitions occur essentially vertically in momentum space. This requirement prohibits the radiative recombination of excitons that have center-of-mass (COM) momentum greater than approximately zero. However, the additional particles in higher-order exciton complexes (e.g., trions and biexcitons), facilitate a recoil effect that allows these complexes to radiate while having high COM momentum. While not directly relevant to the experimental work presented in this thesis, this effect enables the spectroscopic measurement of the temperature of biexciton populations on ultrafast timescales, which will likely be included in future work to better understand additional details of how excited states thermalize. Here, I summarize the recoil effect and the impacts it has on the photoluminescence lineshape of the exciton complexes.

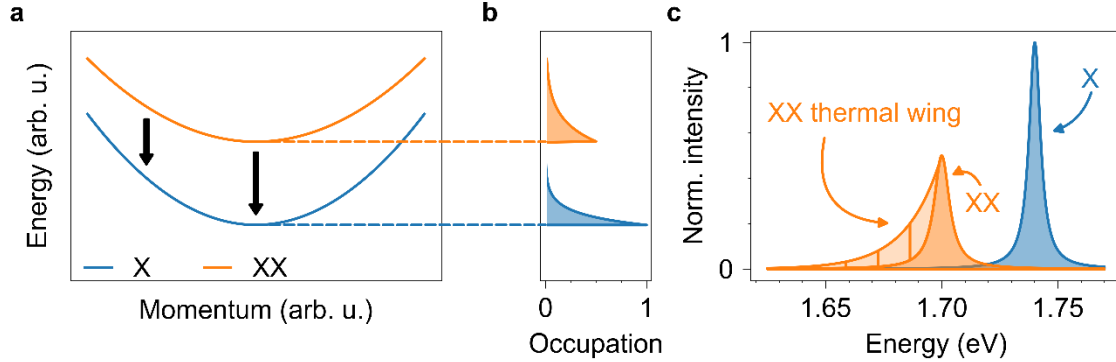


Figure 1.10– Recoil broadening and the formation of a low-energy thermal wing on the PL emission line of an exciton complex (XX). (a) The dispersion of the exciton complex (XX) and constituent excitons (X). The increased mass of the exciton complex flattens the dispersion compared to the lighter constituents. (b) Thermal occupation of the states. Critically, some of the XX population is spread to states above the band minimum. (c) A schematic of the PL line shapes. Both X and XX exhibit a homogenous luminescence line shape that is symmetric, while XX develops a low-energy asymmetry due to the recoil effect. The thermal wing is significantly exaggerated in this cartoon.

In contrast to the limiting effect that momentum conservation has on the radiative recombination of excitons, momentum conservation during radiative recombination for higher-order complexes is relaxed by the recoil of the remaining particles after radiative recombination. Radiative recombination of an exciton complex involves the production of a photon via the recombination of one electron-hole pair while the remaining constituent particles are shifted to the dispersion of their respective subpopulation^{45, 114}. Take, for example, the recombination of charged biexcitons that consist of a trion bound to an exciton. During recombination, one electron-hole pair recombines, and the remaining trion recoils. More precisely, and neglecting the momentum of the emitted photon, momentum conservation demands that the trion has the same center-of-mass momentum as the initial charged biexciton. Yet, the discrepancy in the trion and charged biexcitons masses means that the transition energy depends on the center-of-mass momentum of the charged biexciton due to the differences in the curvatures of the charged biexciton and trion dispersions.

Consequently, the energy of the emitted photon will be *redshifted* by an amount commensurate with the energetic separation of the constituent bands at a given center-of-mass momentum. The luminescence line shape develops a low-energy tail that is reflective of the temperature of the thermal distribution of a given exciton complex in momentum space, the dispersion of the complex under investigation, and the dispersion of the complex that recoils. Figure 1.10 shows a schematic summary of this process.

1.11 Kinetic and Thermodynamic Models

Thermodynamic models of coupled exciton populations provide frameworks in which to interpret luminescence data. Here I provide additional context to the work presented in later chapters.

As the temperature of the semiconductor is lowered, the (charged) excitons and biexcitons stabilize. Consequently, the excited state population is redistributed across the accessible manifolds of (charged) exciton and biexciton states. The details of how the excited state population thermalizes can substantially affect the PLQY; a basic material property that captures the probability that excited states reemit light after photoexcitation. More precisely, and relevant to the experimental work presented in a later chapter, the PLQY for a given exciton sub-population is the product of the formation efficiency of the constituent exciton sub-population and its radiative efficiency. This section provides an overview of two commonly used thermodynamic/kinetic frameworks: master rate equations that can employ temperature-dependent scattering rates^{115, 116} (i.e., Arrhenius-type rate models) and models that treat the exciton sub-populations as thermalized quantum gasses⁴⁴ (i.e., Saha-type models).

Master rate models explicitly define the relaxation rates and coupling terms between sub-populations. In these models, temperature dependence is imposed by the inclusion of non-radiative

scattering channels that depend on the thermal distribution of phonons, often through Bose or Boltzmann factors. The direct access that master rate models give to the coupling terms enables, e.g., the estimation of the PLQY via straightforward analysis of the constituent rates. Furthermore, master rate equations can capture non-equilibrium effects that inherently preclude thermalized gas models since they explicitly retain the time-dependent evolution of the populations. These considerations make master rate equations a particularly appealing framework to interpret time-dependent spectroscopic and transport measurements where non-equilibrium effects and non-linear scattering channels contribute significantly.

Master rate equations have been applied to capture many phenomena in 2D semiconductors. They have been used to model exciton drift under the influence of material strain¹¹⁷, confirm nonclassical exciton diffusion¹¹⁸, and model near-unity quantum yield¹¹⁵. In the Supporting Information of later chapters, we employ master rate equations to analyze the power of the scaling relationship between exciton populations and the density of photoexcitations in addition to qualitatively reproducing super-linear decay kinetics associated with Auger recombination.

On the other hand, thermalized gas models treat the exciton populations under the assumption that there is no net exchange of particles between the coupled sub-populations. In other words, the chemical potential of each exciton population is fixed in such a way that captures the thermodynamic equilibrium between excitons and biexcitons⁴⁴. The appropriate quantum statistics can be readily included to find the equilibrium distribution of particles across the various manifolds of available states. Quantum gas models have the distinct advantage of accounting for quantum effects that alter the phase-space filling of the constituent populations at very high densities and/or

low temperatures. Gas models also enable the analysis of the equilibrium conditions as the temperature of each exciton population varies independently. This is a subtle feature that can capture heating due to carrier-carrier scattering and generalizes the notion of the temperatures of excited states beyond the assumption that thermalization only occurs through heat exchange with the crystal lattice.

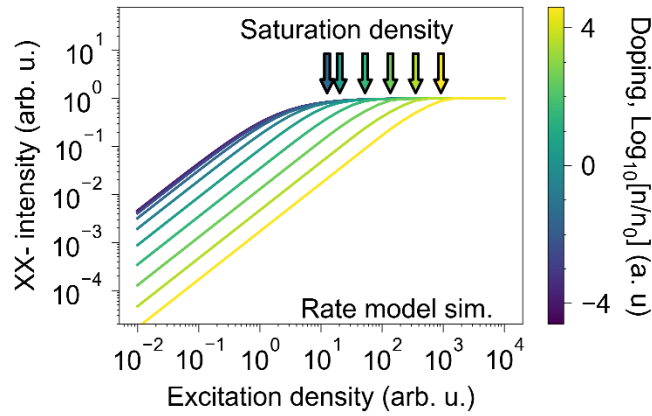


Figure 1.11 – Rate model simulations that demonstrate the sensitivity of the charged biexciton saturation density on the doping level. The Charged biexciton intensity is shown as a function of excitation density for various doping levels (colors) spanning 8 orders of magnitude. The arrows mark the point at which the intensity reaches 80% of the maximum for each curve.

An ongoing point of investigation is the saturation behavior of the charged biexciton at elevated excitation densities. I have made preliminary experimental observations that suggest that the saturation density of the charged biexciton is independent of the degree of electron doping in the semiconductor host. Specifically, these measurements characterized the excitation power-dependence of the charged biexciton in three samples with varying levels of n-doping. Yet, these observations are incongruent with the predictions made by standard rate models, as shown in the simulations presented in Figure 1.11. In typical rate models (such as the ones used to produce the simulations in Figure 1.11), the saturation behavior of charged excitons and biexcitons is captured

as a dramatic reduction in the formation rate of the state as the free electron density decreases. As free electrons are bound to the neutral exciton complexes to form charged states, the formation rate commensurately decreases. Consequently, the saturation level is uniquely defined by the doping level, which I have found to be incongruent with the preliminary experimental results.

On the other hand, quantum gas models provide an alternative perspective. In short, the saturation behavior of the charged biexciton is a consequence of the degeneracy pressure within the *fermi* gas of charged biexcitons. The pinning of the exciton and charged biexciton chemical potentials combined with the degeneracy pressure in the charged biexciton gas results in preferential filling of the exciton population at elevated densities—a purely quantum mechanical result that does not depend on the degree of n-doping. While this result is qualitatively simple, experimental confirmation necessitates a careful systematic study of the saturation behavior in a high-quality and electrostatically gated device. This experiment has, until recently, been beyond our fabrication capabilities.

1.12 Introduction to Quantum Emitters in 2D Semiconductors

Recent technological advancements have accelerated innovations in quantum sensing¹¹⁹ and key distribution¹¹⁹. Technologies built upon the quantum nature of light are particularly appealing. In these schemes, photons are treated as the quantum bits that underlie the gain in computational power of the quantum system over classical analogs. These technologies often leverage the quantum nature of *single* photons and *entangled* photon pairs, which exhibit quantum properties that are absent in ensemble states of light. Consequently, these technologies require the development of reliable sources of quantum light, otherwise known as quantum emitters (QEs).

Mature QE platforms include ultra-cold atoms^{120, 121} and nonlinear optical media in which spontaneous parametric down-conversion or spontaneous four-wave mixing processes herald single photons^{122, 123}. Yet, these platforms have significant drawbacks associated with large infrastructures that limit scalability and indeterministic timing. They also lack integrability with on-chip photonic platforms which necessitate the miniaturization and deterministic nanoscale positioning of QEs, which has spurred a flurry of research into developing next-generation QEs based on solid-state platforms that satisfy the requirements of device miniaturization and deterministic nano-scale positioning, on-demand generation (i.e., triggerability), high-temperature operation, brightness, etc.

Solid state QEs^{48, 124} include color centers in wide bandgap semiconductors such as diamond and silicon carbide, rare-earth impurities in crystals, semiconductor nanostructures, and localized band-edge excitons in 2D semiconductors. Color centers in wide bandgap semiconductors and rare earth impurities in crystals are particularly appealing for quantum transduction applications where the ability to optically initialize quantum states with long coherence times is directly leveraged for computations or quantum memories. On the other hand, excitons localized in semiconductor nanostructures and 2D materials are well suited for the rapid and on-demand generation of single photons that are subsequently manipulated on-chip by downstream photonic systems for computation.

In the following sections, I overview the state-of-the-art of the proposed QE formation mechanisms in 2D semiconductors. A topical overview of experimental observations is also provided throughout.

1.13 Quantum Emitter Formation in 2D Semiconductors

The details of QE formation in 2D semiconductors are not unambiguously established. Since the first experimental observations in 2015^{26, 125-128}, there has been a tremendous amount of breadth in the optical, structural, magnetic, and electrical properties of 2D QEs reported in the literature. QEs have been observed at the edges of 2D flakes, in bubbles¹²⁹ and wrinkles¹³⁰, near plasmonic nanostructures¹³⁰, and in regions irradiated by focused ion beams¹³¹. Unlike more mature QE platforms (e.g., rare-earth ions in crystals and NV centers in diamond) a clear nanoscopic model for 2D QE formation remains mostly elusive. However, some theoretical frameworks unite the majority of experimental observations^{111, 132}, and nanoscale characterization is beginning to provide key experimental insight into the origins of certain classes of 2D QEs¹³³.

A nearly ubiquitous property of 2D QE systems is the presence of large and inhomogeneous material strain. 2D vdWs materials can withstand an astounding amount of tensile strain, up to a deformation of $>10\%$ ³⁷. For example, 2D QEs were first observed in bubbles and wrinkles in mechanically exfoliated 1L-WSe₂. During fabrication, the 2D material is placed in contact with the supporting substrate. Interfacial contaminants are forced to migrate along the interface due to the attractive force between the 2D material and substrate, leading to the coalescence of nano- and micro-scale bubbles underneath the 2D material^{134, 135}. The deformation of the 2D sheet caused by the interfacial bubbles results in large gradients of inhomogeneous strain. Beyond the deformation that occurs on the microscale, recent near-field optical measurements augmented by state-of-the-art atomistic simulations have also revealed the formation of fine wrinkles that exhibit sharp radii of curvature¹³⁴ around the periphery of the bubbles. Beyond bubbles and wrinkles, QEs are observed in systems that utilize engineered nanoscale stressors. Even in systems where strain

is not intentionally used to induce QEs, e.g., at points of contact between the 2D TMD and patterned metallic nanostructures¹³⁰ it has been suggested that nanoscale strain still plays a critical role in QE formation.

Consequently, the current state-of-the-art understanding of QE formation in 1L-WSe₂ comprises two dominant mechanisms: (i) localization of excitons due to nanoscale strain alone¹¹¹ and (ii) efficient pumping of shallow defects via exciton funneling and subsequent hybrid exciton-defect quantum emission¹³². The latter mechanism (ii) is generally the most widely accepted as it provides a microscopic rationale for the emergence of the extremely bright QEs that are commonly observed in experiments.

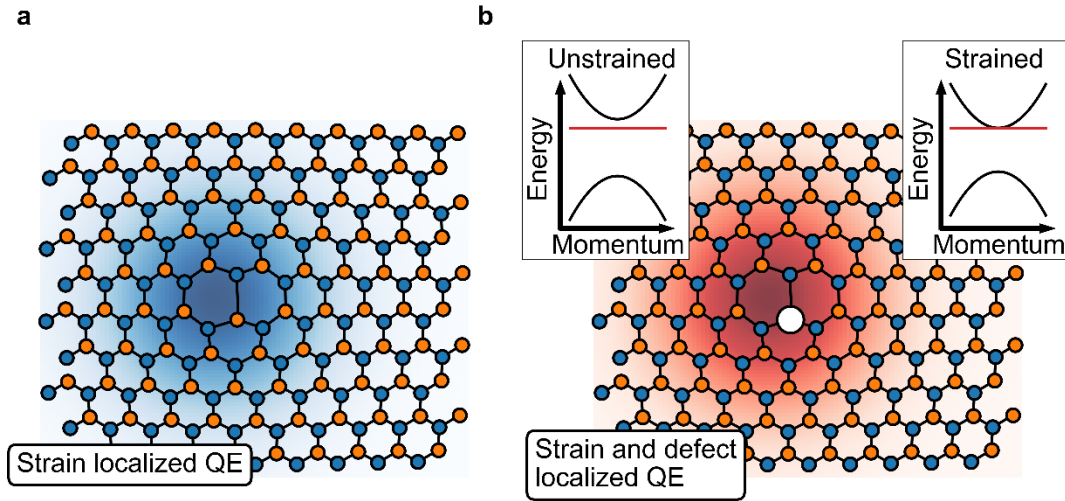


Figure 1.12 – Schematic of quantum emitters (QE) in 2D materials. (a) A strain localized Exciton and (b) a strained Exciton that hybridizes with a shallow donor level. Inset are diagrams of the conduction and valence bands (black) and the defect level (red).

Critical to QE formation is the tunability of the bandgap energy in the presence of strain and its effects on exciton transport. In particular, inhomogeneous material strain can induce a directional flow of excitons. This effect is known as exciton funneling¹³⁶. The variation in atomic

spacing of the underlying semiconductor crystal lattice in the presence of strain results in commensurate changes in the overlap of the atomic wavefunctions which modulates the magnitude of the bandgap energy. Generally, tensile strain (i.e., stretching of the unit cell) closes the bandgap while compressive strain (i.e., compression of the unit cell) opens the bandgap. Consequently, the energy of excitons is also modulated by strain. Excitons are subject to a drift force that is proportional to the spatial variation of the bandgap energy that causes excitons to flow towards regions of higher tensile strain¹¹⁷. Some examples of high-strain regions are the apex of bubbles or hyperfine wrinkles that form around the periphery of otherwise large, microscopic deformations. It is hypothesized that 2D QEs form near these highly strained regions.

Via the modulation of the bandgap energy, appropriate nanoscale uniaxial or biaxial tensile strain is predicted to form 1D or 0D confinement potentials, respectively. An outstanding question is if strain alone can localize single excitons and efficiently produce single photons.

Defects augment strain localization by providing point-like atomic states in which the electron can reside. With sufficient strain, the dark exciton in 1L-WSe₂ becomes resonant with shallow donor states, e.g., Se vacancies¹³², which induce strong coupling with the defect level. In the area surrounding the QE, the long-lived dark exciton population funnels to the location of the Se vacancy, efficiently pumping the strongly localized hybrid state. Additionally, since the crystal defect can only support one excitation at a time, subsequent radiative emission results in the emission of a single photon. Figure 1.12 shows a schematic of a strain localized exciton and a hybrid strained exciton and defect emitter.

1.14 Quantum Emitter Lifetime and Linewidth

The reported excited state lifetimes of quantum emitter in 2D materials vary widely, but generally range from a few hundreds of picoseconds to a few nanoseconds, with some reports of microsecond lifetimes¹³⁷. The extreme variability in the lifetimes is likely a reflection of the competition of localization mechanisms in 2D materials.

For example, the hybrid dark exciton/defect QE tends to exhibit accelerated radiative dynamics relative to the spin-dark exciton due to the relaxation of spin conservation during radiative recombination¹³² due to the the defect breaking the crystal symmetry. Hybridization between the conduction band and defect levels localizes the electron on the defect site which hosts degenerate spin states, enabling the efficient radiative recombination of the defect-localized electron and the valence band hole.

A more general analysis of the lifetime of localized excitons not in the presence of electronic defect levels found that the structural details of the confinement potential (e.g., width, depth, etc.) can strongly modify the radiative lifetime¹¹¹. Essentially, in the presence of a confinement potential that exceeds the exciton Bohr radius ($\approx 1-2$ nm, and as is often predicted for strain fields in real materials) the center-of-mass motion of the exciton is mixed into harmonic oscillator-like states. Consequently, the localized center-of-mass wavefunction acquires high-momentum Fourier components that reduce the radiative rate compared to unlocalized excitons. Unsurprisingly, these effects depend sensitively on the details of the confinement potential. Highly inhomogeneous samples such as the systems consisting of 1L-WSe₂ on Au nanocone arrays that are studied later in this thesis exhibit PL spectra that are qualitatively like what is predicted for systems consisting of excitons localized by random strain potentials. Interestingly, the measured

excited state lifetimes of the localized emitters in the 1L-WSe₂/Au cone samples are substantially more homogeneous than the predictions from the disorder model.

Beyond elucidating the microscopic nature of the QE, the lifetime is of great practical importance. The lifetime of the emitter ultimately limits the emission rate of single photons and defines the uncertainty of light emission after triggering. On the other hand, as the lifetime is extended, the coherence time of the quantum state is also commensurately enhanced. While not necessarily critical for system architectures that do not utilize the QE for quantum transduction, the wide variability of QE properties observed in 2D materials is promising for a myriad of on-chip QE applications. Finally, it is worth noting that the QE lifetime and associated kinetics is a profitable metric to differentiate QE populations in different emitter platforms (see later chapters).

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CHAPTER 2

METHODS

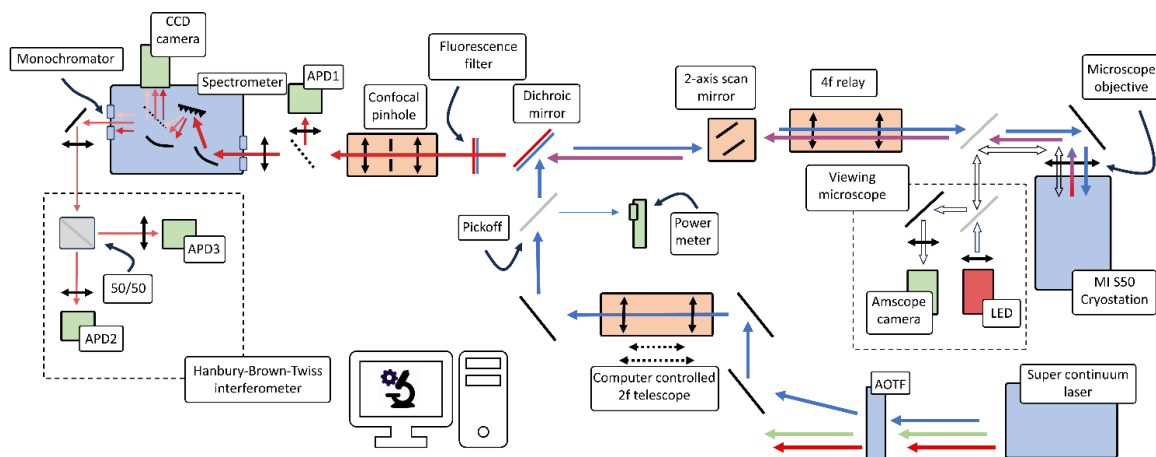


Figure 2.1 – Block diagram of the custom laser-scanning confocal microscope used to conduct the experimental work in this thesis. Colored arrows denote the propagation of light and its approximate color. Black double arrows are lenses. Black solid lines are mirrors. Dashed black lines are flip mirrors. Grey solid lines are beam splitters.

The bulk of the experimental work of this thesis focused on low-temperature steady-state and time-resolved photoluminescence (PL) spectroscopy. To conduct these experiments, I constructed a custom fluorescence microscope. Figure 2.1 presents a block diagram of the microscope and shows some of the custom capabilities that augment its basic functionality. These custom capabilities include automated control of the excitation conditions during excitation spectroscopies, spectrally resolved time-correlated single photon counting, and hardware orchestration using a custom software package.

The microscope is built around a Montana Instruments s50 Cryostat. The s50 is a closed-cycle liquid helium cryostat with a base temperature of 3.1 K. The sample chamber is designed to permit optical access to the sample such that optical imaging and spectroscopy can be performed while the sample is held at the base temperature. In our unit, the sample chamber is

configured with a low-work distance (LWD) module, which raises the sample mount close to the bottom of the outermost window of the chamber. This configuration allows the sample to be brought into focus with an externally mounted microscope objective (typically; Nikon, 40 $\times$, ELWD objective with an NA of 0.6 and an adjustable correction for spherical aberration).

Fluorescence imaging is achieved by scanning the focused laser spot across the surface of the sample. The spot is shifted on the sample by changing the angle at which the laser beam enters the back aperture of the objective. The beam is deflected by a 2-axis scan mirror positioned at the front nodal point of a 4f imaging system and towards the microscope objective which is positioned at the rear nodal point of the 4f system¹. This precise alignment ensures that the deflection of the scanner changes the angle of the beam entering the objective while not shifting the position of the center of the beam away from the back aperture.

The microscope can be operated with many different laser systems. These systems include a tunable femtosecond pulsed laser (Coherent Chameleon-Discovery), a 532 nm continuous wave (CW) diode (Cobalt Samba), a 633 nm CW HeNe (Thorlabs), and a supercontinuum fiber laser (NKT Photonics SuperK Extreme). Most of the work presented here utilized the supercontinuum laser. Yet, it is worth mentioning that the femtosecond pulsed laser enables second-harmonic-generation measurements and when used in conjunction with a streak camera, the measurement of ultrafast fluorescence dynamics. The CW lasers enable Raman characterization and CW photoluminescence. Together with the supercontinuum laser, many different optical measurements are possible.

The microscope has a reconfigurable suite of detectors that includes a Czerny-Turner optical spectrometer (Horiba iHR320) with a scientific CCD camera (Andor iDus 416) and

multiple single-photon avalanche photodiodes (APDs; manufactured by MPD Photonics and Excilite Technologies). Photoluminescence (PL) is measured by directing light into the spectrometer where it is dispersed and detected by the scientific CCD camera. Hyperspectral imaging is achieved by acquiring PL as the beam is scanned across the sample. Spectrally resolved time-correlated single photon counting experiments are conducted by filtering the light with the monochromator exit port on the spectrometer and relaying it to APDs. A single APD is aligned to the monochromator to conduct time-resolved PL (TRPL; in other words, excited-state lifetime measurements) whereas a Hanbury-Brown-Twiss interferometer is aligned to the monochromator to conduct second-order intensity correlation measurements (i.e., $g_2(\tau)$ measurements).

This combination of lasers and detectors built around the 4 K cryostat makes the microscope a versatile characterization tool for 2D material research.

2.1 Selected Technical Details of the Quantum Optical Microscope

2.1.1 Custom Vacuum System for the s50 Cryostat

The chamber of the cryostat is outfitted with a high vacuum turbo pump. The turbo pump increases the total pumping power of the cryostat to ensure that a high vacuum is maintained in the chamber. The turbo pump is an Alcatel ATP 80 and is connected to the chamber with a standard stainless steel high vacuum bellow (KF25 fittings, 6' length, approx.) and a custom KF25-adaptor manufactured by Montana Instruments. The turbo pump, controller, and dry scroll forepump are mounted on a movable cart that is parked next to the optics table and cryostat.

The factory configuration of the s50 cryostat utilizes a diaphragm pump located in the control unit to rough the chamber before the cryopump is turned on. In our system, the diaphragm pump has been disconnected and the built-in Pirani gauge (Series 211 Stinger™ Convection

Vacuum Gauge) has been moved out of the control unit and mounted directly on the back of the head of the cryostat. Two additional cold-cathode ionization gauges are used to monitor the pressure at the chamber and the inlet of the turbo pump. Finally, there is a safety valve located between the turbo pump and the dry scroll pump (Newport series 145 vacuum sentry). The safety valve automatically closes in the event of a power outage to prevent substantial backflow into the chamber. The safety valve automatically opens once the pressure is equalized across the safety valve.

2.1.2 Troubleshooting Vacuum Leaks

Troubleshooting vacuum leaks are an unfortunate reality of conducting low-temperature measurements. If a leak is significant enough it can be detected as an increase in the pressure at the chamber after extended pumping. For example, the typical pressure in the chamber after reaching 4 K is nominally 5×10^{-7} - 1×10^{-6} mbar. A large leak will raise the pressure in the chamber a significant amount (to 1×10^{-5} mbar, for example). However, leaks are often small enough that the pressure change at the gauges is insignificant. In these cases, leaks become apparent when a thin layer of ice forms on the surface of the sample. Ice is identified by a change in the color of the sample surface when heated. The ice is typically composed of Nitrogen and will sublime at around 50 K. Rarely, ice persists at temperatures greater than 200 K. In these cases, the ice is likely composed of water.

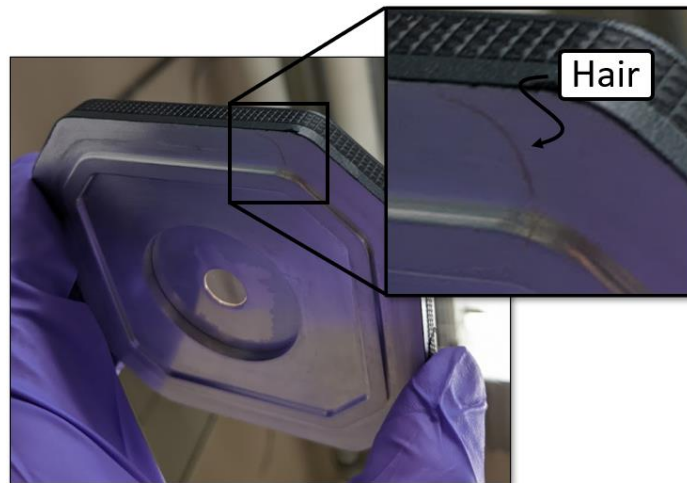


Figure 2.2 – Hair on the lid of the cryostat.

Once a leak is detected, the system should be warmed and vented. The O-Rings that seal the chamber should be carefully inspected for debris. It may be prudent to remove the O-Rings, wipe them clean with a dry Kim wipe, inspect them for cracking, and regrease them with a light coat of high vacuum grease (Apiezon L ultra high vacuum grease) before reinstallation. If the O-rings are damaged, they should be replaced (McMaster-Carr P/N: 5267T133). The mating surfaces on the chamber lid and the PCB board in the chamber should also be inspected for debris and cleaned if necessary. Figure 2.2 shows a photograph of a hair on the bottom of the chamber lid that caused a large vacuum leak. Debris smaller than the hair shown in Figure 2.2 has also resulted in leaking. After inspecting and cleaning the O-rings, we typically cool down a low-value sample to test the system.

The next most-common point of failure is the outer window in the low working distance module. This window is in the chamber lid. The seal around the window can be broken when the window is rammed by the microscope objective. Obvious damage to the window seal as is not common. Rather, a window might leak without any visible damage. So, it is prudent to replace the

low working distance window module if cleaning the O-rings does not fix the leak. A new low working distance module (P/N: 4100-1725, uncoated F.S. LWD vacuum window assembly) should be ordered immediately from Montana Instruments to ensure that the lab has a new unit on-hand in the event of a failure.

If the leak persists, the KF connections in the vacuum line that connects the chamber to the inlet of the turbo should be cleaned and regreased. Beyond that, I recommend using a Helium leak detector to pinpoint the location of the leak. Using the Helium leak detector requires specialized training that is beyond the scope of this thesis. Good luck.

2.1.3 Super Continuum Laser Pulse Shape

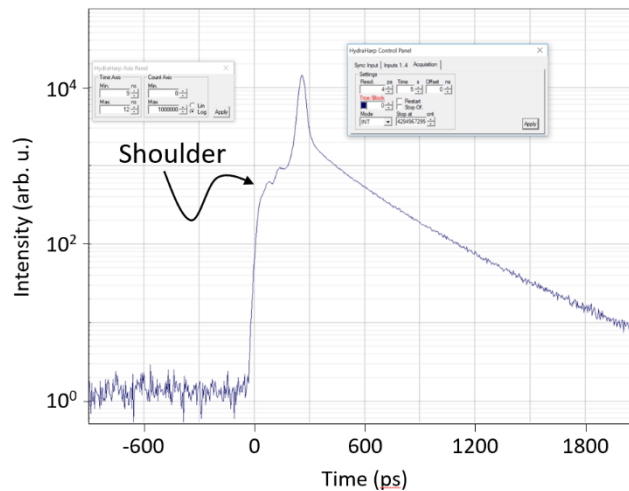


Figure 2.3 – Pulse shape of the supercontinuum laser. The supercontinuum laser pulse is measured by directing laser light onto a single-photon avalanche photodiode and building up a histogram of detection events relative to the seed pulse that generates the super continuum.

A super continuum laser (NKT photonics SuperK EXTREME EXW-12) is used in the time-correlated single photon counting experiments presented in this thesis. The resolution of the measurements is often limited by the pulse duration of the laser. The laser is specified to have a

pulse width of 55 ps full width at half maximum, yet the pulse is not symmetric in time. There is a prominent shoulder that precedes the main pulse, as shown in Figure 2.3. The shoulder is observable in some of the excited-state lifetime measurements discussed at length in Chapter 4. NKT confirmed that this shoulder is expected and is a consequence of the complexity of generating supercontinuum light.

2.2 Photoluminescence Excitation Spectroscopy

Photoluminescence excitation spectroscopy (PLE) constitutes a large portion of the journal article presented in Chapter 3. We developed a PLE technique to measure the excitation spectrum of the relative photoluminescence quantum yields (PLQYs) of excitons and biexcitons in a 2D semiconductor, 1L-WSe₂. The measurement technique augments standard PLE by maintaining constant photoabsorption and excitation density by (i) tuning the excitation power following an electromagnetic simulation of the sample stack and (ii) maintaining a constant area of illumination by systematically tuning the collimation of the laser before it is coupled into the microscope. Here, I first motivate the development of the PLE measurement with a discussion of the PLQY in the presence of biexcitons, supplemented by basic rate model analysis. Then, I discuss the details of the electromagnetic simulations and how the laser beam is prepared to maintain a constant illumination area on the sample. Finally, I will discuss the additional experimental details of the PLE calibrations.

2.2.1 Photoluminescence Quantum Yields in the Presence of Biexcitons

The photoluminescence quantum yield (PLQY) is the efficiency at which a semiconductor reemits light after optical excitation. It is the ratio of the number of photons emitted to the number

of photons absorbed. In conventional semiconductor systems and at low photoexcitation densities, the PLQY can be approximated by analyzing a simple rate equation with linear population dynamics,

$$\frac{dN}{dt} = -(k_{rad} + k_{non-rad})N$$

$$PLQY = \frac{k_{rad}}{k_{rad} + k_{non-rad}}$$

Where N is the pair density of electrons and holes, k_{rad} is the radiative recombination rate, and $k_{non-rad}$ is the non-radiative recombination rate. The PLQY is found by calculating the ratio of the radiative rate to the sum of all rates that depopulate N . The PLQY captures the competition between radiative and nonradiative relaxation channels at the band edge in conventional semiconductors.

The strong Coulomb interaction in 2D semiconductors leads to the stabilization of sub populations of excitons. The relative PLQY of each sub population is sensitive to the strengths of the relaxation pathways that branch from the initial photoexcited population. The sensitivity of the PLQYs to the competing formation rates can be demonstrated by analyzing a simple rate model consisting of three coupled populations,

$$\frac{dN_1}{dt} = I - (k_{1 \rightarrow 2} + k_{1 \rightarrow 3})N_1$$

$$\frac{dN_2}{dt} = k_{1 \rightarrow 2}N_1 - (k_{2,rad} + k_{2,non-rad})N_2$$

$$\frac{dN_3}{dt} = k_{1 \rightarrow 3}N_1 - (k_{3,rad} + k_{3,non-rad})N_3$$

Where N_i is the *density* of the i^{th} population, $k_{i \rightarrow j}$ are coupling constant between the i^{th} and j^{th} population, and $k_{(i,(non-))rad}$ are the (non-)radiative relaxation rates for the i^{th} population. The

initial population, N_1 , is pumped by the driving function, I , which represents an optical pump (i.e., the laser). N_1 subsequently branches to the subpopulations N_2 and N_3 . The PLQYs for N_2 and N_3 are,

$$PLQY_{N_2} = \frac{k_{1 \rightarrow 2}}{k_{1 \rightarrow 2} + k_{1 \rightarrow 3}} \times \frac{k_{2,rad}}{k_{2,rad} + k_{2,non-rad}}$$

$$PLQY_{N_3} = \frac{k_{1 \rightarrow 3}}{k_{1 \rightarrow 2} + k_{1 \rightarrow 3}} \times \frac{k_{3,rad}}{k_{3,rad} + k_{3,non-rad}}$$

The PLQY for N_1 is zero because there is not a radiative decay pathway included in its relaxation dynamics. The state-resolved PLQY can also be expressed as the product of the branching probability and the probability of radiative recombination,

$$PLQY_{N_2} = P\{1 \rightarrow 2\} \times P\{2 \rightarrow Y\}$$

$$PLQY_{N_3} = P\{1 \rightarrow 3\} \times P\{3 \rightarrow Y\}$$

The first term on the right-hand side is the strength of the branching ratio from N_1 . The second term on the right-hand side is the probability of radiative relaxation.

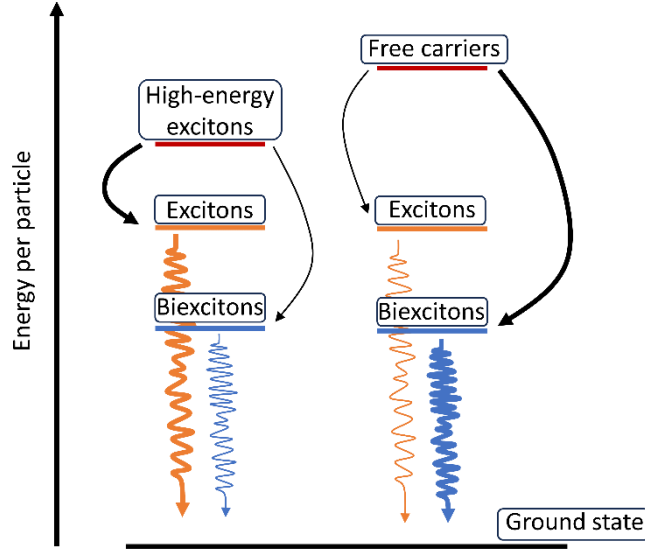


Figure 2.4 – Energy level diagram showing the branching of an initial population of high-energy excitons (left) or free carriers (right) to exciton and biexciton population that subsequently luminesce. The strength of the relaxation pathways from the initial population corresponds to the weight of the arrows that connect the populations.

The second definition emphasizes the importance of the branching ratio in the definition of the PLQY for a specific state. Our experimental work focuses on precisely characterizing the relative change in the branching ratio as the photoexcitation energy is changed. Specifically, we have measured the excitation energy dependence of the PLQYs of excitons and biexcitons. Figure 2.4 shows an energy level diagram that illustrates that the branching ratio depends on whether high-energy excitons (left) or free carriers (right) are photoexcited. The figure illustrates a model in which biexcitons are more efficiently pumped after the excitation of free carriers, leading to an overall increase in the biexciton PL intensity.

In the presence of biexcitons, the rate model can be modified to include a quadratic coupling term between N_1 and N_3 ,

$$\frac{dN_1}{dt} = I - k_{1 \rightarrow 2} N_1 - A \times k_{1 \rightarrow 3} N_1^2$$

$$\frac{dN_2}{dt} = k_{1 \rightarrow 2} N_1 - (k_{2,rad} + k_{2,non-rad}) N_2$$

$$\frac{dN_3}{dt} = k_{1 \rightarrow 3} N_1^2 - (k_{3,rad} + k_{3,non-rad}) N_3$$

The quadratic coupling term from $N_1 \rightarrow N_3$ modifies the model to incorporate the dynamics of a biexciton population (N_3) and an exciton population (N_2). A is the area of illumination. The PLQY for N_2 is then,

$$PLQY_{N_2} = \frac{k_{1 \rightarrow 2} N_1}{k_{1 \rightarrow 2} N_1 + A \times k_{1 \rightarrow 3} N_1^2} \times \frac{k_{2,rad}}{k_{2,rad} + k_{2,non-rad}}$$

$$PLQY_{N_2} = \frac{k_{1 \rightarrow 2}}{k_{1 \rightarrow 2} + A \times k_{1 \rightarrow 3} N_1} \times \frac{k_{2,rad}}{k_{2,rad} + k_{2,non-rad}}$$

And the PLQY for N_3 is,

$$PLQY_{N_3} = \frac{A \times k_{1 \rightarrow 3} N_1^2}{k_{1 \rightarrow 2} N_1 + A \times k_{1 \rightarrow 3} N_1^2} \times \frac{k_{3,rad}}{k_{3,rad} + k_{3,non-rad}}$$

$$PLQY_{N_3} = \frac{A \times k_{1 \rightarrow 3}}{k_{1 \rightarrow 2} N_1^{-1} + A \times k_{1 \rightarrow 3}} \times \frac{k_{3,rad}}{k_{3,rad} + k_{3,non-rad}}$$

This analysis demonstrates that the branching ratio depends on N_1 when the coupling terms $N_1 \rightarrow N_2$ and $N_1 \rightarrow N_3$ have a different dependence on the initial population (N_1). In the limit of large N_1 ,

$$PLQY_{N_2} \rightarrow \frac{k_{1 \rightarrow 2}}{k_{1 \rightarrow 2} + A \times k_{1 \rightarrow 3} N_1} \times \frac{k_{2,rad}}{k_{2,rad} + k_{2,non-rad}} \approx 0 \times P\{2 \rightarrow \gamma\} = 0$$

$$PLQY_{N_3} \rightarrow \frac{A \times k_{1 \rightarrow 3}}{k_{1 \rightarrow 2} N_1^{-1} + A \times k_{1 \rightarrow 3}} \times \frac{k_{3,rad}}{k_{3,rad} + k_{3,non-rad}} \approx 1 \times P\{3 \rightarrow \gamma\} = P\{3 \rightarrow \gamma\}$$

Figure 2.5 complements the rate model analysis above by showing that the fraction of the total excited state population that are biexcitons is increased with increasing excitation density.

The spectra are normalized to the exciton PL emission to exemplify the super-linear growth of the biexciton emission features.

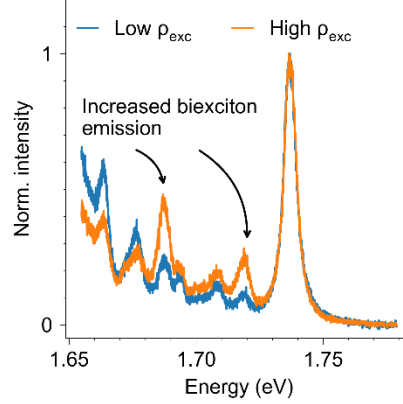


Figure 2.5 – Experimental examples that demonstrate the need to maintain a constant excitation density (ρ_{exc}) to measure the PLQY of biexcitons. Comparison of typical PL spectra of 1L-WSe2 encapsulated in hBN at 4 K at low excitation density (blue; 10^{10} cm^{-2}) versus high excitation density (orange; 10^{11} cm^{-2}). The relative PL intensity of the neutral and charged biexcitons is increased with increasing excitation density.

We also control the total photoabsorption during the PLE measurement. Controlling the total photoabsorption allows us to use the intensity of each emitter to measure the relative changes the PLQY of each state at different excitation energies and can be demonstrated by again analyzing the simple rate model consisting of three coupled populations,

$$\frac{dN_1}{dt} = I - k_{1 \rightarrow 2}N_1 - k_{1 \rightarrow 3}N_1$$

$$\frac{dN_2}{dt} = k_{1 \rightarrow 2}N_1 - (k_{2, \text{rad}} + k_{2, \text{non-rad}})N_2$$

$$\frac{dN_3}{dt} = k_{1 \rightarrow 3}N_1 - (k_{3, \text{rad}} + k_{3, \text{non-rad}})N_3$$

The PLQY for N_3 is,

$$PLQY_{N_3} = \frac{k_{1 \rightarrow 3}}{k_{1 \rightarrow 2} + k_{1 \rightarrow 3}} \times \frac{k_{3, \text{rad}}}{k_{3, \text{rad}} + k_{3, \text{non-rad}}}$$

Yet, the photoluminescence intensity is what is actually measured during the experiment,

$$I_{N3} = PLQY_{N3} \times N_{tot}$$

where N_{tot} is the total number of photons that are absorbed during the duration of the measurement. We are particularly interested in how $PLQY_{N3}$ depends on photoexcitation energy (e.g., $E_{exc} = E_1$ and E_2) at a given excitation density ($\rho_{exc} = \rho_0$). So, we measure I_{N3} at $E_{exc} = E_1$ and $E_{exc} = E_2$ while maintaining $\rho_{exc} = \rho_0$,

$$I_{N3}(E_{exc} = E_1, \rho_{exc} = \rho_0) = PLQY_{N3}(E_1, \rho_{exc} = \rho_0) \times N_{tot}(E_1)$$

And,

$$I_{N3}(E_{exc} = E_2, \rho_{exc} = \rho_0) = PLQY_{N3}(E_2, \rho_{exc} = \rho_0) \times N_{tot}(E_2)$$

The ratio of the intensities is,

$$\frac{I_{N3}(E_{exc} = E_1, \rho_{exc} = \rho_0)}{I_{N3}(E_{exc} = E_2, \rho_{exc} = \rho_0)} = \frac{PLQY_{N3}(E_1, \rho_{exc} = \rho_0) \times N_{tot}(E_1)}{PLQY_{N3}(E_2, \rho_{exc} = \rho_0) \times N_{tot}(E_2)}$$

The ratio of the intensities precisely encodes the energy dependence of the state-resolved PLQY if the total number of excitations are the same at each excitation density.

$$\frac{I_{N3}(E_{exc} = E_1, \rho_{exc} = \rho_0)}{I_{N3}(E_{exc} = E_2, \rho_{exc} = \rho_0)} = \frac{PLQY_{N3}(E_1, \rho_{exc} = \rho_0)}{PLQY_{N3}(E_2, \rho_{exc} = \rho_0)}; \text{ if } N_{tot}(E_1) = N_{tot}(E_2)$$

Combined, control of the photoexcitation density accounts for the changes to the branching ratio due to biexcitons while control of the total photoabsorption allows the relative PLQYs to be measured by comparing the PL intensity at different excitation energies. This approach is the foundation of the measurement; (i) maintaining constant photoabsorption and (ii) maintaining constant excitation density while varying the excitation energy and measuring the PL intensity of excitons and biexcitons.

Finally, the measurement becomes sensitive to only the branching ratio if the radiative efficiency does not depend on the photoexcitation energy,

$$\frac{I_{N3}(E_1, \rho_0)}{I_{N3}(E_2, \rho_0)} = \frac{P\{E_1, \rho_0; 1 \rightarrow 3\}}{P\{E_2, \rho_0; 1 \rightarrow 3\}},$$

$$\text{if } N_{tot}(E_1) = N_{tot}(E_2) \text{ and } P\{E_1, \rho_0; 3 \rightarrow Y\} = P\{E_2, \rho_0; 3 \rightarrow Y\}$$

Relative changes in the branching ratio are detected as changes in the PL intensity when the total photoabsorption and excitation density are held constant, and the radiative efficiency does not depend on photoexcitation energy. The relationship derived above means that the PLE measurement can be used to probe the complex microscopic physics that underpins the details of the branching ratio and the formation of excitons and biexcitons.

2.2.2 Overview of the Photoabsorption Calibration

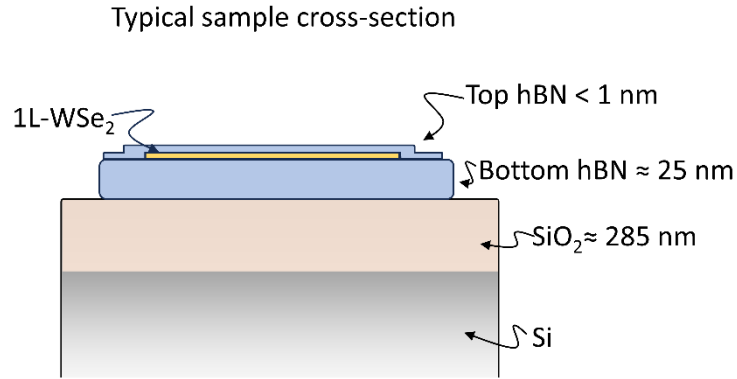


Figure 2.6 – Cross sectional schematic of a typical hBN/1L-WSe₂/hBN sample.

To conduct the PLE measurement, it is essential to have a realistic estimate of the energy-dependent photoabsorption across the measurement window of the experiment. Yet, the intensity of the laser at the 1L-WSe₂ is altered by the layered architecture of the sample, as shown in Figure 2.6. The sample consists of a thin layer of hBN (< 1 nm) that encapsulates the 1L-WSe₂ (0.7 nm)

that is supported by a crystallite of hBN (25 nm) and all placed on a standard silicon wafer (285 nm of SiO₂ on Si). The degree to which the intensity of the laser varies over a range of wavelengths depends on the interplay between its wavelength, the thicknesses of the layers in the sample, and the dielectric functions of materials. Interference effects strongly alter the optical field intensity at the 1L-WSe₂ since the thickness of the sample stack is on the order of the wavelength of the laser. Careful quantification of these interference effects necessitates the use of an electromagnetic model so that they can be compensated for during the experiment. Figure 2.7 demonstrates that PLE spectra is significantly distorted when these interference effects are neglected by comparing PLE spectra with and without the interference correction factor applied during the experiment. The data in Figure 2.7 was adapt from previous work conducted by Borys, Schuck, et al., *ACS nano*, 2017 which carefully quantified the shape of the linear PLE spectra of 1L-MoS₂ supported by a Si/SiO₂ substrate. Previous works by other groups^{2, 3} had reported that the PLE spectrum of 1L-MoS₂ decreased sharply at elevated excitation energies. These reports did not account for interference effects.

We addressed the interference effects in our layered samples (c.f. Figure 2.6) by utilizing a transfer matrix method (TMM) to solve the absorption by the 1L-WSe₂ embedded in the stack. To calculate the total absorption by the 1L-WSe₂, the TMM is used to find the electric and magnetic fields within the stack. Next, the net energy absorbed by the 1L-WSe₂ layer is found by calculating the Poynting vector from the fields found by the TMM calculation. The TMM proceeds by assuming that (i) the sample is a multilayer stack of dielectric media and (ii) the incident field is a normally incident plane wave. In each intermediate region, forward and backward propagating waves are allowed. In the last region, there is only a forward propagating wave. The transfer matrix

is constructed from the matching conditions imposed by the continuity of the fields at each boundary. The reflection and transmission amplitudes are found by solving the linear equations defined by the transfer matrix which relate the transmitted and reflected electric and magnetic fields. The fields at every point are found by backward (forward) propagating the transmitted field (total field in the first layer) into the stack using a partial transfer matrix.

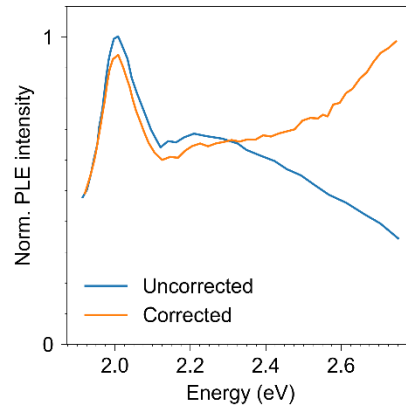


Figure 2.7 – Comparison of the linear PLE spectrum of 1L-MoS2 with and without correction for photonic cavity effects. Data is adapted from Borys, Schuck, et al., ACS nano, 2017, 11, 2, 2115-2123.

In practice, we use an open-source numerical implementation of the TMM that has been developed in the Python programming language^{4,5}. However, I will give a derivation of the TMM for dissipative media since most standard texts^{6,7} do not provide detailed discussions that see the calculation through to the power absorbed in each layer.

2.2.3 Derivation of the Transfer Matrix Method for Dielectric Thin Films

The complex index of refraction in layer j , $\tilde{n}_j$, is defined as,

$$\tilde{n}_j = c\sqrt{\mu_j\epsilon_j}$$

$$\tilde{n}_j = n_j + i\kappa_j$$

Where κ is the extinction coefficient.

And the complex wavenumber, $\tilde{k}_j$,

$$\tilde{k}_j = \tilde{n}_j \frac{\omega}{c}$$

The complex wave impedance, Z_j , is a convenient quantity to define for the TMM analysis. Z_j is derived by analyzing the relationship between the electric and magnetic fields in a dissipative medium.

$$Z_j = \sqrt{\mu_j / \epsilon_j}$$

The magnitude of Z_j relates to the amplitudes of the fields whereas the phase of Z_j alters the phase relationship between the two fields.

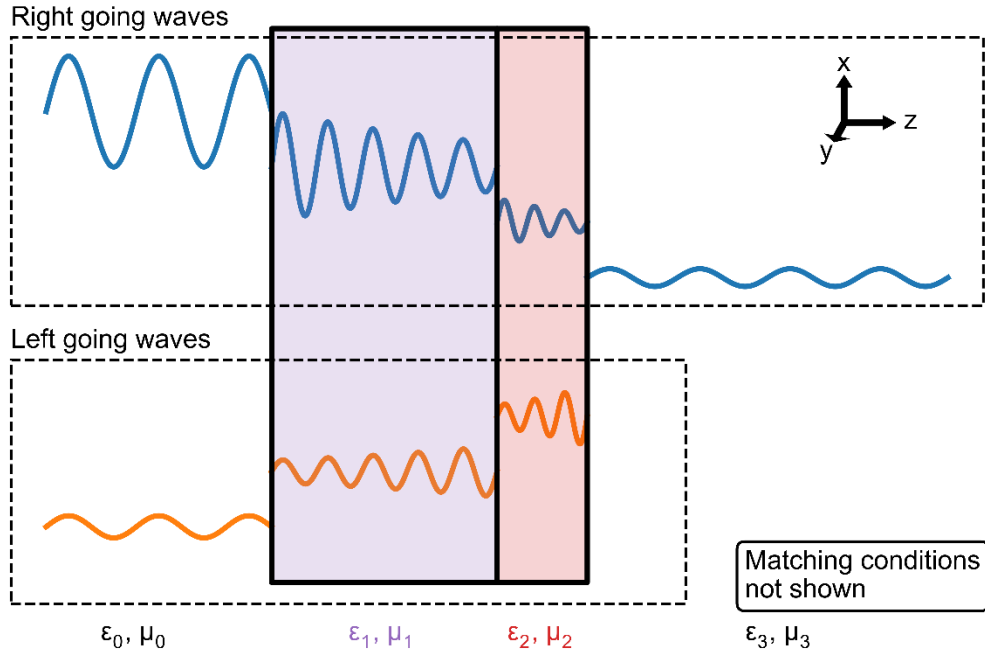


Figure 2.8 – Schematic of the propagating plane waves that are used in the transfer matrix method for dielectric thin films under coherent optical illumination. Each region has a complex permittivity and permeability (ϵ_j, μ_j). The waves are not matched at each interface in this schematic.

The fields within each layer consist of a right and left propagating wave with amplitudes E^+ and H^+ (right going) and E^- and H^- (left going). Figure 2.8 shows a schematic of the propagation of the left and right-going plane waves. The field amplitudes within the region are found by propagating the waves across the region. For instance, the electric field amplitude at the right boundary of the region, j , is,

$$E_j(z = \text{Right boundary}) = E_j^+ + E_j^-$$

The electric field amplitude at the left boundary is,

$$E_j(z = \text{Left boundary}) = E_j^+ e^{-i\tilde{k}_j d_j} + E_j^- e^{+i\tilde{k}_j d_j}$$

Where the right propagating wave was backward propagated to the left boundary, the left propagating wave was forward propagated to the left boundary, and d_j is the thickness of the layer.

Now consider the fields on either side of a boundary such as at the boundary between material $j-1$ and j . For simplicity, set the location of the boundary to $z = 0$. The fields must be continuous across the boundary because there are no free charges or currents. The fields at the right side of region $j - 1$ are,

$$E_{j-1}(\text{Right boundary}) = E_{j-1}^+ + E_{j-1}^-$$

$$H_{j-1}(\text{Right boundary}) = H_{j-1}^+ + H_{j-1}^-$$

The fields at the left side of region j are,

$$E_j(\text{Left boundary}) = E_j^+ e^{-i\tilde{k}_j d_j} + E_j^- e^{+i\tilde{k}_j d_j}$$

$$H_j(\text{Left boundary}) = H_j^+ e^{-i\tilde{k}_j d_j} + H_j^- e^{+i\tilde{k}_j d_j}$$

Matching the electric fields at the boundary, and dropping the (...) notation,

$$E_{j-1} = E_j$$

$$\begin{aligned}
&= E_j^+ e^{-i\tilde{k}_j d_j} + E_j^- e^{+i\tilde{k}_j d_j} = (E_j^+ + E_j^-) \cos(\tilde{k}_j d_j) - i(E_j^+ - E_j^-) \sin(\tilde{k}_j d_j) \\
&= E_j \cos(\tilde{k}_j d_j) - iZ_j H_j \sin(\tilde{k}_j d_j)
\end{aligned}$$

The last step utilized Maxwell's equation to relate the left and right propagating electric field waves to the magnetic field. Matching the magnetic field at the boundary gives,

$$H_{j-1} = H_j \cos(\tilde{k}_j d_j) - iZ_j^{-1} E_j \sin(\tilde{k}_j d_j)$$

Together,

$$E_{j-1} = E_j \cos(\tilde{k}_j d_j) - iZ_j H_j \sin(\tilde{k}_j d_j)$$

$$H_{j-1} = H_j \cos(\tilde{k}_j d_j) - iZ_j^{-1} E_j \sin(\tilde{k}_j d_j)$$

In matrix form,

$$\begin{pmatrix} E_{j-1} \\ H_{j-1} \end{pmatrix} = \begin{pmatrix} \cos(\tilde{k}_j d_j) & -iZ_j \sin(\tilde{k}_j d_j) \\ -iZ_j^{-1} \sin(\tilde{k}_j d_j) & \cos(\tilde{k}_j d_j) \end{pmatrix} \begin{pmatrix} E_j \\ H_j \end{pmatrix}$$

There is only a right propagating wave in the last region, N. So,

$$E_N = E_N^+$$

$$H_N = Z_N^{-1} E_N^+$$

E_N^+ is the transmission amplitude, denoted as t . The reflection amplitude, r , is identified as magnitude of the left propagating electric field in the first region, E_0^- . Setting the incident amplitude $E_0^+ = 1$ yields,

$$\begin{pmatrix} 1 + r \\ Z_0^{-1}(1 - r) \end{pmatrix} = \left(\prod_{j=0}^N D_j \right) \begin{pmatrix} 1 \\ Z_N^{-1} \end{pmatrix} t$$

With,

$$D_j = \begin{pmatrix} \cos(\tilde{k}_j d_j) & -iZ_j \sin(\tilde{k}_j d_j) \\ -iZ_j^{-1} \sin(\tilde{k}_j d_j) & \cos(\tilde{k}_j d_j) \end{pmatrix}$$

The reflection and transmission amplitudes (r and t) are found by solving the equation above. The fields at each boundary are readily found by back-propagating the transmitted fields to the desired interface,

$$\begin{pmatrix} E_k \\ H_k \end{pmatrix} = \left(\prod_{j=k+1}^N D_j \right) \begin{pmatrix} 1 \\ Z_N^{-1} \end{pmatrix} t$$

Where the product means,

$$\prod_{j=k+1}^N D_j = D_{k+1} \dots D_{N-1} D_N$$

Finally, the absorption in a layer (for example, layer k) is found by calculating the change in magnitude of the Poynting vector across it,

$$\Delta S_k = |E_{k-1} H_{k-1}|^2 - |E_k H_k|^2$$

The power absorbed by the layer as a fraction of the incident power delivered to the sample stack is,

$$\frac{\Delta S_k}{S_{incident}} = \Delta S_k \left(\frac{\epsilon_0}{\mu_0} \right)$$

2.2.4 Example Implementation of the Transfer Matrix Method

Figure 2.9a shows the complex refractive index for 1L-WSe₂ (4 K), hBN, SiO₂, and Si, used in the TMM calculations in Figure 2.9. The extinction coefficient for 1L-WSe₂ peaks around exciton absorption resonances which are superimposed on continuum absorption. The refractive indexes for hBN, SiO₂, and Si are real-valued with $n \approx 2.1$, 1.5, and 4, respectively.

The photoexcitation external quantum efficiency (EQE) is the number of photons absorbed by the 1L-WSe₂ as a fraction of the number of photons incident on the sample stack. Figure 2.9b

(left) shows the energy-dependent photoexcitation EQE calculated for a sample consisting of a thin supporting crystallite of hBN (25 nm). Figure 2.9b (right) shows the photoexcitation EQE calculated for a sample consisting of a thicker supporting hBN crystallite (50 nm). The capping layer of hBN is 1 nm thick, the 1L-WSe₂ is 0.7 nm thick, and the SiO₂ thickness is 285 nm in both calculations. The photoexcitation EQE for the sample that is supported by the thicker hBN crystallite is reduced at 2.2 eV compared to the thinner sample.

The calculated photoexcitation EQE is used to calibrate the power of the laser to maintain constant carrier injection at each excitation energy. For example, the photoexcitation EQE calibration curve in Figure 2.9b (left) tells us that the laser needs to be about three times as intense at 2.0 eV than when on the resonance at 2.2 eV. The simulations in Figure 2.9b demonstrate the sensitivity of the photoexcitation EQE to the sample geometry and highlight the importance of the photoexcitation EQE in the calibration of the PLE measurement. Further discussion is included in the main text and supporting information in Chapter 3.

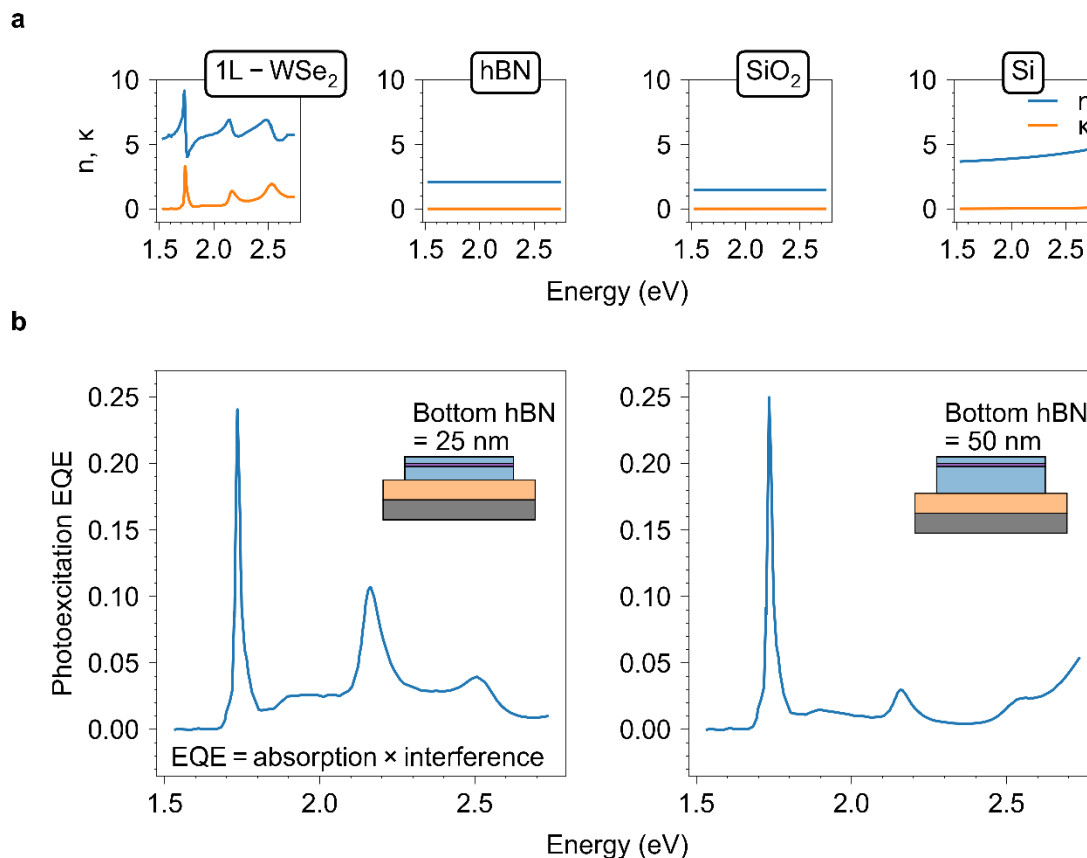


Figure 2.9 – Example photoexcitation external quantum efficiency calculations. (a) the complex refractive indexes of the materials used in the calculations. (b) Example photoexcitation external quantum efficiency calculations done using the transfer matrix method. To demonstrate the sensitivity of the photoexcitation external quantum efficiency to layer thicknesses, the left panel shows the energy dependence of the photoexcitation external quantum efficiency with a sample supported by a thinner (25 nm) hBN crystallite whereas the right panel shows the photoexcitation external quantum efficiency of a sample supported by a thicker (50 nm) hBN crystallite.

2.2.5 Maintaining a Constant Area of Illumination During the PLE Measurement

The collimation of the laser was systematically adjusted to maintain a constant area of illumination during the PLE measurement. The effect that beam collimation has on the illumination pattern of the sample can be demonstrated with Fourier optical analysis. The intensity profile at the sample can be found by (i) modeling the microscope objective as a spherical phase delay and (ii) propagating the field amplitude from the objective to the sample using the Fresnel theory of

diffraction. Following the analysis of⁸, the field distribution in the focal plane of the objective is given by the integral equation,

$$U(u, v) = e^{i\frac{k}{2f}(u^2 + v^2)} \times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} U_l(x, y) P(x, y) e^{-i\frac{2\pi}{\lambda f}(ux + vy)} dx dy$$

In the above expression, u and v are the cartesian coordinates in the focal plane, x and y are the cartesian coordinates at the aperture of the objective, k is the wavenumber, λ is the wavelength, f is the focal length of the objective, U_l is the field amplitude at the aperture of the objective, and $P(x, y)$ is pupil function of the objective. The pupil function is a circle function with a radius corresponding to the physical dimension of the back aperture of the microscope objective. The integral can be converted to circular coordinates to take advantage of the cutoff of the pupil function,

$$U(u, v) = e^{i\frac{k}{2f}(u^2 + v^2)} \times \int_0^a \int_0^{2\pi} U_l(r) e^{-i\frac{2\pi}{\lambda f}(ur \cos(\theta) + vr \sin(\theta))} r d\theta dr$$

where a is the radius of the back aperture of the microscope objective.

Figure 2.10 shows numerical calculations of the field intensity in the plane of the microscope objective as the collimation of the laser is detuned. The collimation is tuned by introducing a curved phase front with a radius of curvature r_c at the objective,

$$U_l(r) = e^{ik\frac{r}{r_c}}$$

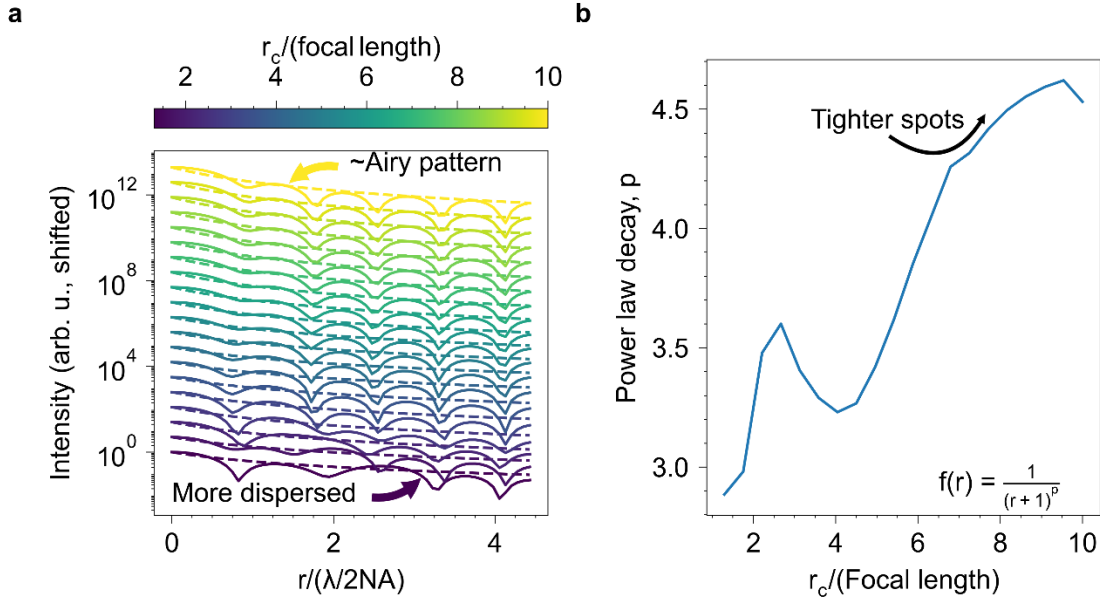


Figure 2.10 – Simulations of the illumination pattern at the sample when the laser beam is systematically uncollimated. (a) Radial distribution of field intensity at the sample as the beam is uncollimated. The darker lines in the waterfall plot correspond to relatively more divergent incident beams than the lighter colors. The dashed lines fit the local maxima of the intensity profile with a power law decay. (b) The strength of the power-law decay extracted from the fitting in panel (a). A larger power law, p , means that the distribution decays at a faster rate.

The calculations in Figure 2.10 show that as the radius of curvature of the incident wave is increased, the spatial extent of the illumination profile gets tighter and approaches an Airy pattern. The spreading of the illumination pattern is quantified by fitting the local maxima of the illumination profile to a power law decay. The results of this fitting are shown in Figure 2.10b. As the point source is moved further away from the objective (i.e., the radius of curvature of the incident spherical wave is increased), the illumination pattern decays more rapidly. The fits demonstrate that the illumination pattern on the sample is enlarged as the collimation of the laser beam is decreased.

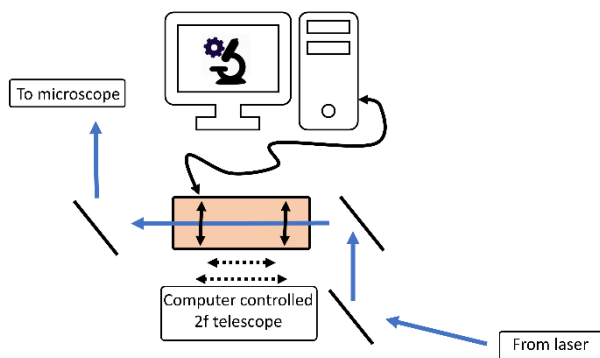


Figure 2.11 – Schematic of the computer controlled 2f (Gaussian) telescope that was used to prepare the collimation of the laser beam before coupling it into the microscope.

In practice, the collimation of the beam is set by empirically measuring the size of the illumination area as the collimation is adjusted. Figure 2.11 shows a schematic of the automated 2f Gaussian telescope that was used to collimate the laser before coupling it into the microscope. The position and angle of the beam are precisely aligned to the translation axis of the telescope by adjusting a series of mirrors just before the telescope. The quality of the alignment is determined by repeatedly translating the stage forward and backward while monitoring the wobble of the centroid of the illumination profile on the sample. The ideal angular alignment is achieved when the centroid of the illumination profile on the sample does not move when either the stage position or the color of the laser is changed. Figure 2.12a shows a photograph of the experimental setup. The front lens in the telescope is mounted on a computer-controlled translation stage. This allows for the systematic control of the lens separation.

Figure 2.12b shows images of the illumination profile for two colors as the separation of the lens in the telescope is changed. As the separation of the lenses moves away from the ideal separation, the width of the illumination profile is enlarged. Critically, these images are acquired while utilizing a consistent portion of the dynamic range of the camera, using an autoexposure

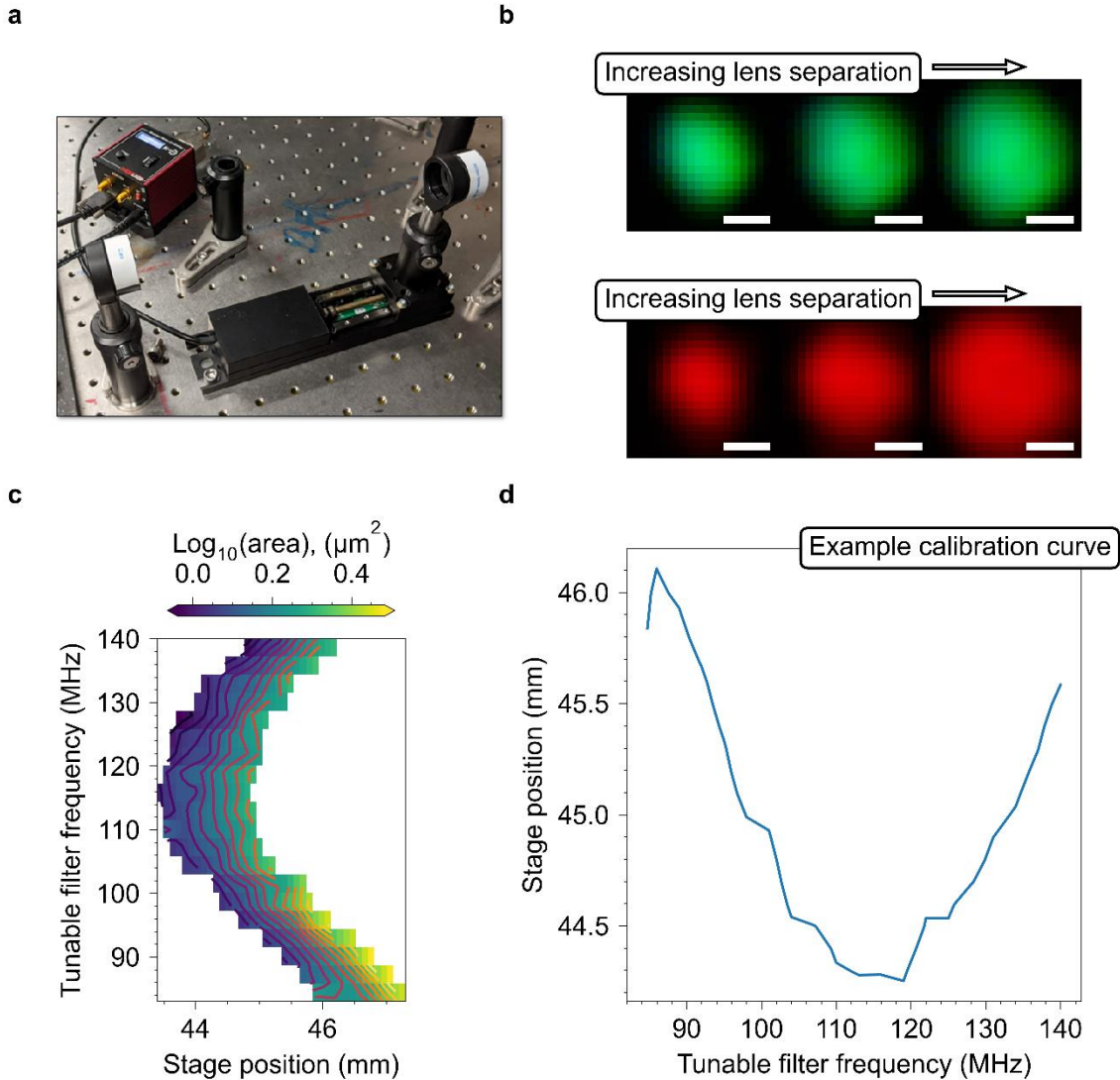


Figure 2.12 – Experimental setup used to maintain a constant area of illumination during the PLE measurement. (a) A photograph of the computer-controlled Gaussian telescope used to tune the collimation of the beam before coupling it into the microscope. The front lens is mounted on a motorized translation stage. (b) A series of 3 images that illustrate the expansion of the illumination profile as the lens separation is increased. Scalebars = 1 μm . (c) a combined contour plot and colormap of the size of the illumination profile as the stage position and laser color (tunable filter frequency) are changed. Higher frequencies correspond to bluer colors. (d) An example stage calibration curve. The calibration curve is a contour extracted from panel (c).

algorithm that adjusts both the exposure time of the camera and the power of the laser to maintain a consistent maximum accumulation of counts below the saturation threshold of the camera. This

autoexposure algorithm ensures that the illumination profile is measured under equivalent exposure conditions.

The size of the illumination profile is found by fitting the images with a two-dimensional Gaussian intensity profile from which the characteristic area is found. The characteristic area is defined as the area of the ellipse subtended by the semimajor and semiminor variances of the fitted intensity profile, as shown in Figure 2.13. Figure 2.12c shows a contour map of the illumination area as a function of the telescope stage position and the color of the laser. The calibration curve for the stage position is extracted from this contour map and presented in Figure 2.10d. The curve in Figure 2.10d defines the necessary position of the stage to maintain a constant area of illumination on the sample.

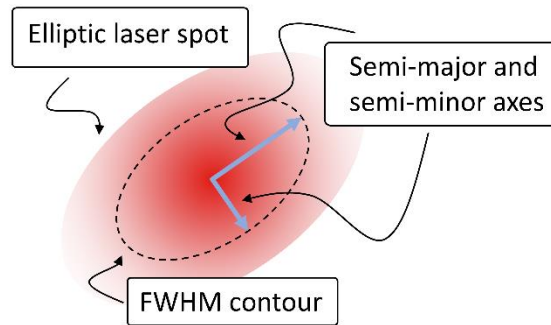


Figure 2.13 – Schematic of a focused laser spot area and of how the spot area is defined. The spot is fitted with a 2D Gaussian intensity profile. From the fit, the characteristic widths are extracted. The characteristic widths define an ellipse that subtends the characteristic widths of the spot. The product of the semi-major (r_1) and semi-minor (r_2) widths of this ellipse define the characteristic area of the spot (i.e., $A = \pi r_1 r_2$).

2.2.6 Calibration of the Acousto-Optic Tunable Filter and Active Power Monitoring

A supercontinuum fiber laser is used for the PLE measurement. The laser outputs broadband white light that spans the visible spectrum. Therefore, spectrally filtering the laser

output is necessary for the PLE measurement. Spectral filtering is achieved with an acousto-optic tunable filter (AOTF). The AOTF is a TeO_2 crystal that is acoustically driven by a radio frequency (RF) source. Figure 2.14 demonstrates the operation of the AOTF and its wavelength selectivity. A Bragg grating is formed by the acoustic waves in the crystal. Incident light that satisfies the Bragg condition is angularly separated from the beam and coupled into the microscope. The passband of the filter is changed by tuning the frequency of the RF source. Consequently, it is necessary to calibrate the relationship between the RF driving frequency and the passband of the filter.

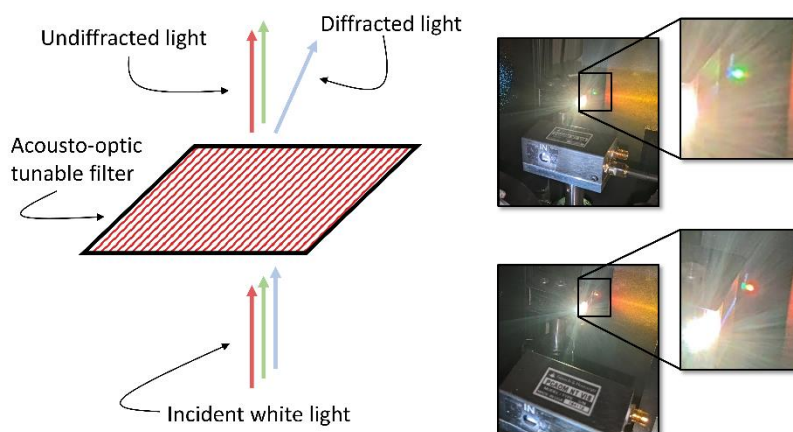


Figure 2.14 – Demonstration of the acousto-optic tunable filter (AOTF) that was used to spectrally filter the supercontinuum laser during the PLE measurements. Left, a schematic of the spectral selectivity of the AOTF. Acoustic waves are launched in the crystal which form a Bragg grating which diffracts a narrow band of light into the microscope. Right, photos of the AOTF tuned to diffract green and red light. The undiffracted white light is dumped into a permanent beam block whereas the diffracted light is blocked by a removable beam block.

The AOTF is calibrated by monitoring the spectrum of the laser light that is passed by the filter while the RF frequency is tuned. The filtered light is relayed to an optical spectrometer for measurement. The calibration for the conversion between RF driving frequency and the passband of the AOTF has been automated by tracking the wavelength of the laser as the RF frequency is

continuously swept. Figure 2.15 shows the spectrum of the laser as the RF frequency is tuned and the resultant calibration curve.

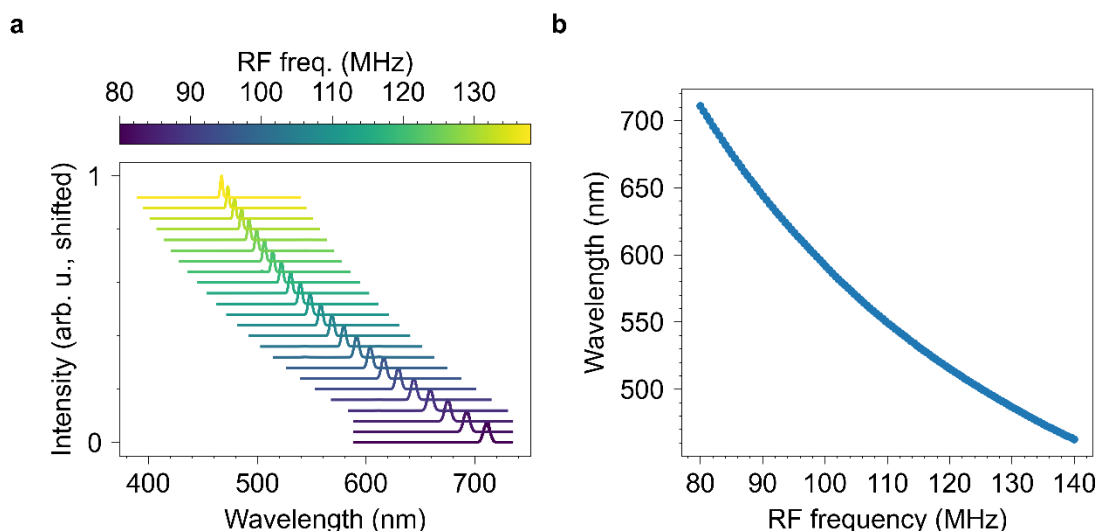


Figure 2.15 – Calibration of the acousto-optic tunable filter. The spectrum of the supercontinuum laser light filtered by the AOTF is measured as the RF driving frequency is tuned. (a) Example RF-frequency-dependent laser spectra. (b) The calibration curve that relates the driving frequency to the center wavelength of the filter passband.

Finally, the power of the laser is adjusted by tuning the power of the RF source that drives the AOTF. The power delivered to the sample depends on factors such as the level of attenuation in the beam path, the collimation of the beam, wavelength dependence of the dichroic mirror that is used to couple the laser into the microscope, losses at each optical element, etc. The calibration is sensitive enough to warrant the implementation of a basic feedback loop to ensure that the power of the beam is set correctly during the PLE measurement. Active monitoring is achieved by placing a pickoff just before the dichroic mirror that couples the beam into the microscope. The pickoff is a thin glass microscope slide placed at an oblique angle to the beam path. The slide reflects approximately 3% of the light onto a power meter that is running during the measurement. The

relationship between the power measured at the position of the pickoff and the power delivered to the sample is calibrated by measuring the power at the pickoff and the power delivered to the outermost window of the cryostat under identical excitation conditions (i.e., attenuation level, alignment, collimation, etc.). The wavelength-dependent conversion between the power at the pickoff position and the power at the sample is measured by sweeping the RF frequency of the AOTF, measuring the power at the pickoff, and repeating the frequency sweep while measuring the power delivered to the sample. Figure 2.16a shows a block diagram that indicates the positions at which the power is measured. Figure 2.16b shows the power conversion calibration curve.

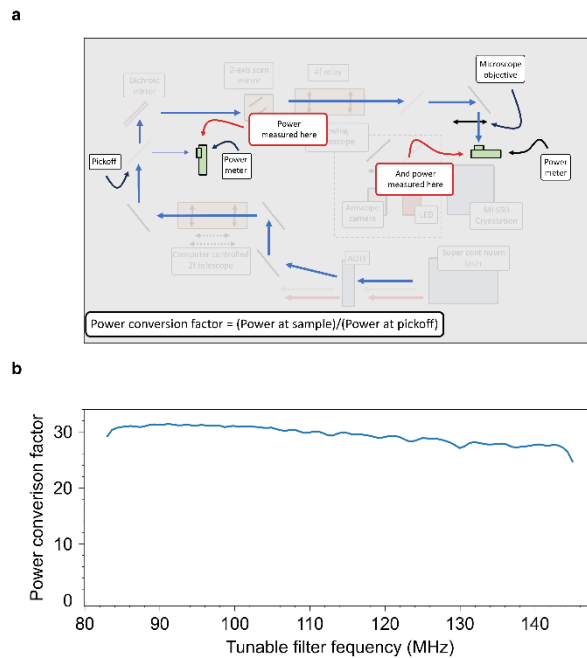


Figure 2.16 –Determination of the conversion factor between the power measured at the pickoff position and the power delivered to the sample. (a) Schematic of the positions at which the power is measured. (b) An example power calibration curve.

With all the calibration curves generated and active power monitoring implemented, the power of the laser can be actively tuned by adjusting the power of the RF driver of the AOTF during the measurement to ensure that the excitation density and total absorption are maintained within the accuracy of the calibrations. The power is adjusted to maintain constant photo absorption according to,

$$\rho_{exc} = \frac{(P[J/s]) \times (Pickoff \text{ to Sample})(6.242 \times 10^{18}[eV/J]) \times (EQE)}{(78 \times 10^6[pulses/s]) \times (E_{exc}[eV]) \times (A[cm^2])}$$

P is the power measured at the pickoff position, *Pickoff to Sample* is the conversion from the power at the pickoff to the power delivered to the sample, EQE is the photoexcitation external quantum efficiency as defined above at the energy of the laser, 78 MHz is the repetition rate of the laser, E_{exc} is the energy per photon of the laser light, and A is the area of illumination. It is worth noting that this definition is the total carrier injection density integrated throughout each pulse (55 ps FWHM).

2.3 Time-Correlated Single Photon Counting (TCSPC)

Time-correlated single photon counting (TCSPC) is the time-resolved detection of a particular color of light emitted from a sample. These measurements entail spectrally isolating a particular emission feature and registering the arrival time of those photons on a detector. In our microscope, spectral resolution is achieved by using the monochromator exit port of the spectrometer and timing resolution is achieved by using single-photon APD detectors in conjunction with commercial ultrafast timing electronics (PicoQuant HydraHarp 400). When a photon is detected by an APD, a signal is transmitted to the HydraHarp. The HydraHarp then registers the arrival time of the event. The operational details of the HydraHarp are well documented in the user manual and

white papers⁹ published by PicoQuant. Figure 2.17 summarizes the two modes of operation that are relevant to the experiments I will discuss: (i) event time-tagging in reference to a global clock (time-tagged time-resolved T2; TTTR T2 mode) and (ii) on-board histogramming of events relative to an external synchronization signal (time-resolved emission spectra; TRES mode). T2 mode is used to measure photon correlations in the HBT interferometer and TRES mode is used to measure excited state lifetimes.

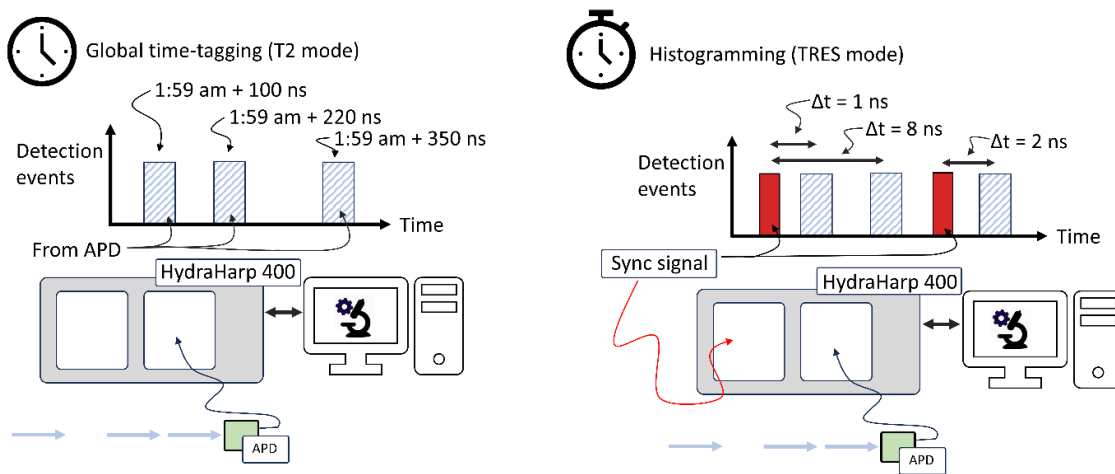
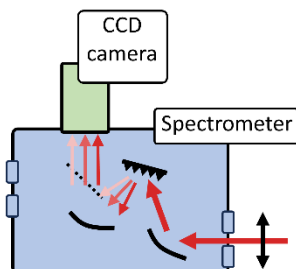


Figure 2.17 – Operational modes of the HydraHarp400. Left, T2 mode; when the avalanche photodiode (APD) detects a photon, the HH400 logs a detection event relative to global clock. Right, time-resolved emission spectra (TRES) mode. In TRES mode, the detection events are registered relative to an external trigger. Usually, the sync signal comes from a photodiode that measures the seed pulse in a pulsed laser.

2.3.1 Optics of the Spectrally Resolved TCSPC Apparatus

Light directed to CCD camera



Light directed to Monochromator

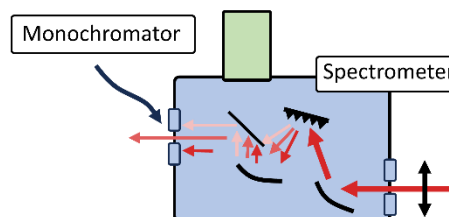


Figure 2.18 – Selectivity of exit port on the iHR320 spectrometer. Left, light is directed onto the spectroscopy CCD camera. Right, an internal mirror directs light through the monochromator exit port.

Figure 2.18 shows how the iHR320 spectrometer can direct light out of a monochromator exit port instead of imaging it onto the spectroscopy CCD. After light is dispersed by the grating in the spectrometer, an internal flip mirror redirects the light towards the monochromator exit port instead of towards the spectroscopy CCD. Then, the light converges onto the exit slit and exits the instrument. Subsequently, it is necessary to relay the light from the monochromator exit port to a detector. The optical relay is achieved by a simple imaging system which images the exit slit of the monochromator onto the detector with a collimating lens and a microscope objective.

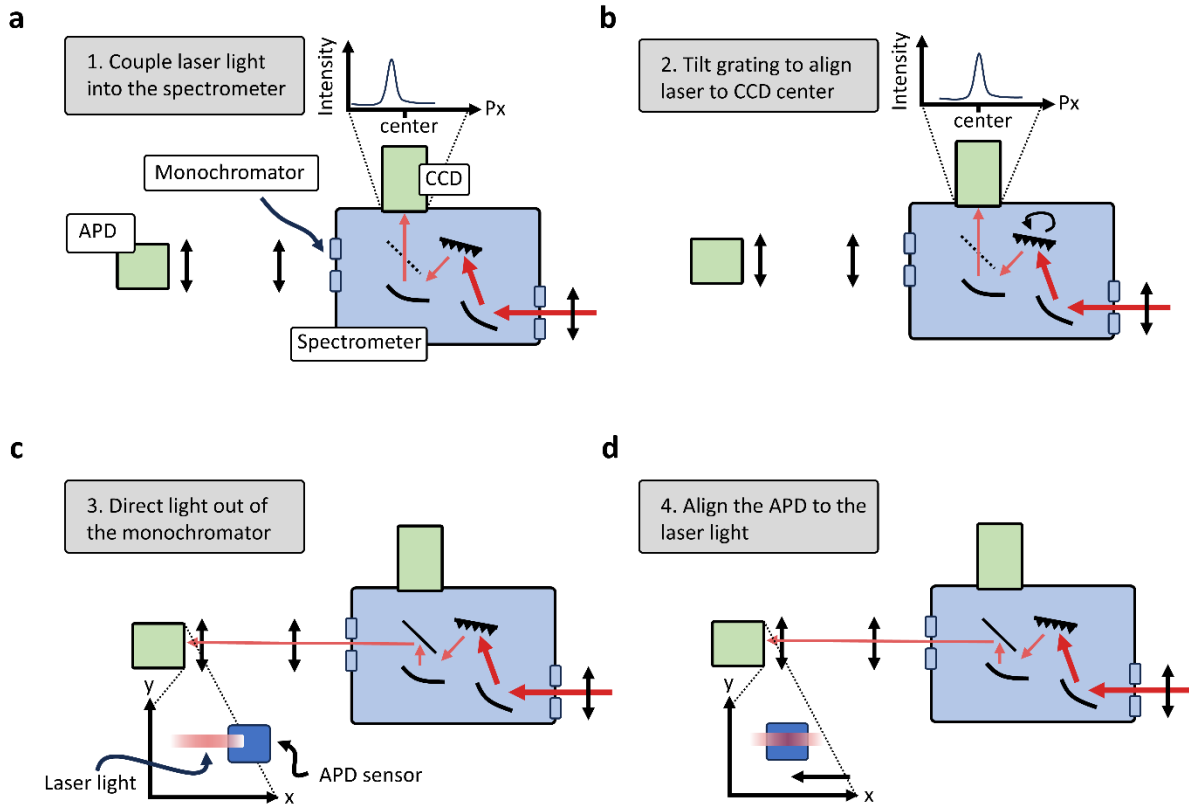


Figure 2.19– Alignment procedure for the spectrally resolved TCSPC apparatus. (a) Laser light is coupled into the spectrometer and measured by the spectroscopy CCD. (b) The tilt angle of the grating is adjusted to position the peak of the laser spectrum on the center of the spectroscopy CCD. (c) The light is directed out of the monochromator exit port and (d) the APD is aligned to the image of the laser light.

The lateral position of the APD in the image plane of the relay determines the wavelength offset between the band center of the spectroscopy CCD and the TCSPC apparatus. The two systems can be coaligned by first positioning narrow band light (e.g., laser light) precisely on the center of the spectroscopy CCD. Then, the same light is directed into the TCSPC setup by flipping the internal mirror, and the APD is aligned to the light in the image plane of the relay. This procedure aligns the TCSPC apparatus to the center of the spectroscopy CCD. That way, an emission feature can be rapidly directed into the TCSPC apparatus by simply rotating the spectrometer grating to align the feature to the center of the spectroscopy CCD and flipping the

internal mirror towards the monochromator exit port. Figure 2.19 shows a diagram of the alignment procedure.

In nearly all cases, the spectral bandwidth of the TCSPC apparatus is limited by the magnification of the optical relay and the physical size of the detection area on the APD rather than the physical width of the exit slit. This is because the APDs are single-pixel detectors with a small detection area (e.g., 50 μm diameter for the MPD APDs) and the magnification of the relay is typically $3\times$ - $5\times$ (from the detector to the exit port). In practice, it is useful to quantify the spectral bandwidth of the TCSPC apparatus in terms of the spatial extent on the spectroscopy CCD mounted to the spectrometer. This way, when the grating resolution is changed, the bandwidth is easily measured by acquiring a spectrum on the camera. For example, if the optical relay has a magnification of $3\times$, the image of the APD at the image plane of the spectrometer is $50\text{ }\mu\text{m} \times 3 = 150\text{ }\mu\text{m}$. The size of the pixels in the Andor Idus 416 is 15 μm . So, the bandwidth is 10 pixels of the spectroscopy CCD regardless of the choice of grating.

2.3.2 Hanbury-Brown-Twiss Interferometry

The Hanbury-Brown-Twiss interferometer (HBT) consists of a 50/50 beam splitter and two single-photon avalanche photodiodes. Light is spectrally resolved by using the monochromator exit port on the spectrometer and directed into the HBT after being collimated. The light then impinges on the 50/50 beam splitter and the light in each arm is focused onto an APD. Figure 2.18 shows a schematic of the HBT. The detection events on each arm of the HBT are registered on separate channels of the time-tagging electronics discussed above (PicoQuant HydraHarp 400). Critically, the HydraHarp is operated in T2 mode, which assigns a time tag corresponding to a

global clock to each detection event. Subsequently, the time-dependent intensities on each arm of the HBT are calculated by time-binning the detection events.

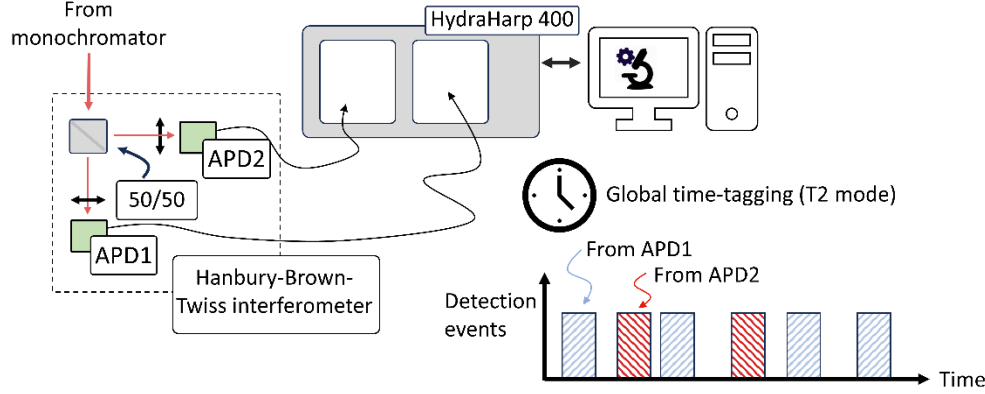


Figure 2.20- Schematic of the Hanbury-Brown and Twiss (HBT) interferometer. Light is incident on a 50/50 beam splitter and then detected by APDs aligned to the exit ports of the beam splitter. The detection events on each arm of the HBT are logged by the HydraHarp in T2 mode (in reference to a global clock). The coincident count rate is calculated as a post-processing step.

The second-order intensity-intensity correlation function is computed by cross-correlating intensity on each arm (denoted 1 and 2) of the HBT,

$$G_2(\tau) = \int_{-\infty}^{\infty} I_1(t + \tau) I_2(t) dt$$

The time-dependent intensities are calculated by binning the detection events on each arm. Usually, the time bins are approximately 0.5 – 5 ns depending on the lifetime of the emitter, timing-resolution of the APDs, and the average count rates. Evidence for single-photon emission occurs when $G(0)$ is less than $G(\tau)$ (i.e., there is a dip in the correlation function at zero time delay) in a phenomenon called photon antibunching¹⁰. At the most basic level, photon antibunching describes a stream of photons that are well separated in time. For example, an emissive trap state cycles between “on” and “off” via the emission of a single photon and subsequent carrier capture, as illustrated in Figure 2.21. The light emitted by such a state is antibunched because the optical fields

generated by the radiative recombination of the single trap are that of a periodic stream of single photons.

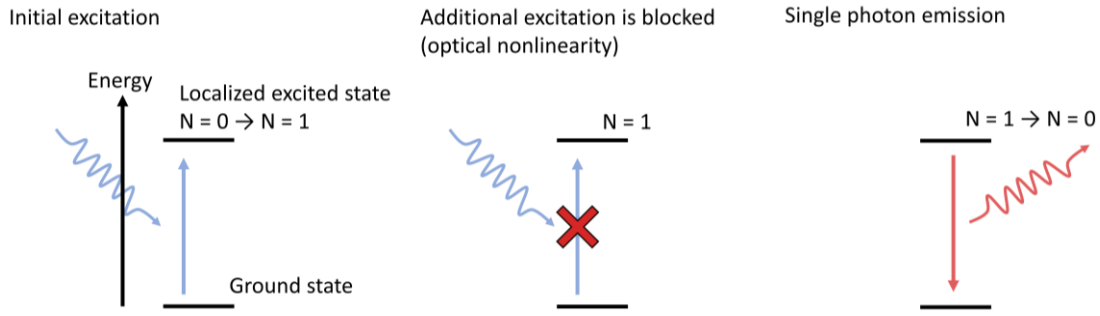


Figure 2.21 – Single photon emission from a localized excited state. Once the state is single occupied ($N = 1$) additional excitation cannot occur. The state eventually relaxes via the emission of a single photon before additional excitation can occur.

Therefore, the beam splitter in the HBT splits one of these single photons into a superposition state with amplitude evenly distributed across the two arms of the HBT. Consequently, the measurement of the photon by one of the APDs collapses the superposition state.

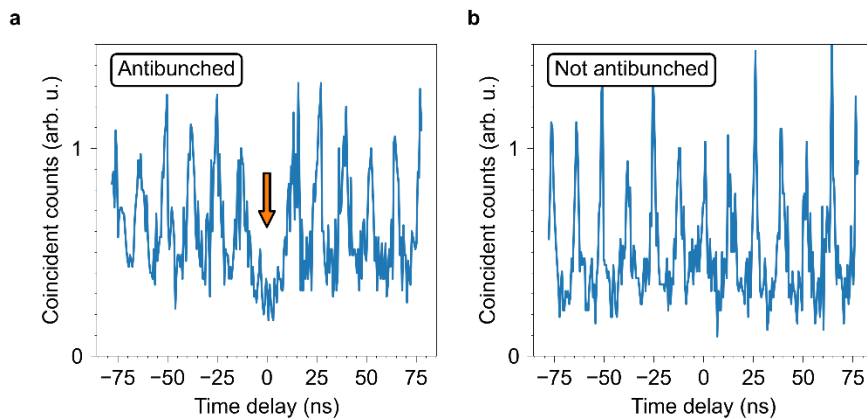


Figure 2.22 – Experimental signatures of antibunching. (a) A pulsed g_2 curve that shows an antibunching dip. (b) A pulsed g_2 curve that does not exhibit signatures of antibunching.

The second-order correlation function for a stream of single photons exhibits an antibunching dip at short time delays.

Figure 2.22 shows the coincident count rates (which are proportional to $g_2(\tau)$) for antibunched versus classical light. A pulsed laser was used in these measurements, so the antibunching dip is observed as a missing peak in the pulse train of $g_2(\tau)$.

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CHAPTER 3

INCREASE OF TRION AND CHARGED BIEXCITON PHOTOLUMINESCENCE
QUANTUM YIELDS BY ABOVE-GAP EXCITATION IN
SINGLE-LAYER WSe₂

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Abstract

Two-dimensional (2D) semiconductors stand at the forefront of a wide breadth of areas in nanoscale and quantum optoelectronics. In these materials, strong optical responses are married to many-body systems with intense coulombic interactions and a rich suite of excitonic phenomena. Whether excited optically or electronically, in the steady state or out of equilibrium, thermalization from an initial population to lower-energy excitons is ubiquitous in these systems. Here, enabled by meticulous excitation spectroscopies, we show that the photoluminescence quantum yields of charged biexcitons and trions in single-layer WSe₂ are enhanced by up to 12× as the excitation energy is swept from below to above the quasiparticle bandgap. Insight into the origin of the enhancement is gained by power- and temperature-dependent measurements, elucidating key mechanisms including the formation of KQ excitons, direct formation of trions and biexcitons from an electron-hole gas/plasma, and defect-trapping. A robust foundation for future investigations that correlate ultrafast phenomena with the enhancement is established. This first-of-its-kind dataset reveals a compelling complexity of excited state relaxation in 2D semiconductors, provides critical insight for the continued development of carrier thermalization models, and highlights the potential to modulate excitonic yields and probe out-of-equilibrium physics with 2D semiconductors.

Introduction

Due to strong confinement and intense coulombic interactions, two-dimensional (2D) monolayer transition metal dichalcogenides (1L-TMDs) are rich excitonic systems that have proven valuable for investigating fundamental light-matter interactions¹⁻⁵, harvesting light on the nanoscale^{6, 7}, generating quantum states of light⁸⁻¹⁰, and probing non-equilibrium physical systems^{11, 12}. At low temperatures, an extensive suite of bound states emerges in 1L-TMDs, consisting of bright and

dark¹³⁻¹⁵ (charged) excitons and biexcitons^{16, 17}. Whereas excitons are hydrogen-like bound states between conduction band electrons and valence band holes, biexcitons are molecular-like bound states of two excitons. In 1L-WSe₂, two biexciton species prevail at cryogenic temperatures. The first is the neutral biexciton^{17, 18}, which is a four-particle bound state consisting of two excitons. The second is a charged biexciton¹⁹⁻²² that is composed of the neutral biexciton with an additional bound charge. Under appropriate conditions (e.g. doping, encapsulation, material quality, etc.) these biexcitons are highly emissive and dominate the photoluminescence of 1L-WSe₂¹⁹⁻²², making them attractive systems in which to study exciton-exciton interactions in the regime of strong coulombic interactions. In addition, the biexcitonic states are appealing for optoelectronic and quantum photonic applications where phenomena such as cascaded photon-pair emission^{23, 24} and inverted valley polarization²⁵ can be directly integrated with the gate tunability of charged exciton complexes^{19-22, 26}.

Because of the intense many-body interactions, the formation of exciton and biexciton complexes in 1L-WSe₂ (and other TMD semiconductors) from an initial non-equilibrium state is a non-trivial process that influences any effort to harness their potential for technological application. Optical excitation of 1L-TMDs—even if only resonant with a single excitonic state—ultimately generates a diverse population of exciton complexes^{19-22, 26} and free carriers that depend on factors such as the energy and density of the optical excitation as well as the doping level, lattice temperature, strain, and surrounding dielectric environment of the 1L-TMD. While a body of knowledge exists about how these factors effect single excitons²⁷⁻²⁹, significant gaps exist in understanding their roles in the non-equilibrium formation of exciton complexes such as the charged excitons (i.e., the inter-and intra-valley trions)³⁰ and biexcitons.

Here, we report that the generation and resulting photoluminescence intensity of charged exciton complexes (trions and charged biexcitons) in 1L-WSe₂ are significantly enhanced with increasing excitation energy. Comprehensive and precisely controlled energy- and power-dependent optical spectroscopy indicates that the enhanced emission from the charged complexes is due to an increase in their photoluminescence quantum yields with increasing energy. The increase in the quantum yield exhibits a threshold-like behavior, occurring at the same photoexcitation energy that corresponds to the creation of an initial free-carrier (electrons and holes) gas. Such differences between exciton formation from free carriers versus an exciton gas have been previously investigated in 2D semiconductors^{27, 28, 31, 32} and 2D quantum well systems^{33, 34}, but have been restricted to single exciton states and dynamics, neglecting to address impacts on quantum yields. Additional temperature-dependent characterization reveals signatures that momentum distribution of excitons and/or charge capture by defects may also contribute to the enhanced quantum yields. These results provide experimental insights that build on the results of ultra-fast optical^{28, 32} and momentum-resolved³⁵ spectroscopic techniques, showing how the initial state created by optical excitation alters the ultimate population of excitons and multiexcitons, highlighting the non-trivial nature of thermalization in 2D semiconductors.

Results

Excitation-Energy-Dependent Linear and Nonlinear Formation of Excitons

Depending on the incident photon energy, photoexcitation of 1L-TMD semiconductors can excite excitons directly via their Rydberg resonances^{4, 36-38} or indirectly through a low-energy continuum of states that spans the exciton resonances or a high-energy continuum of unbound free-carrier

states^{32, 37-39}. Figure 1 demonstrates that these different excitation pathways alter the relative populations of exciton complexes in n-doped 1L-WSe₂ that is encapsulated by top- and bottom-layers of hBN. The photoluminescence spectra at 4 K after photoexcitation at low energy (1.83 eV) and high energy (2.33 eV) at identical excitation densities are compared in Figure 1a. The low-energy photoexcitation results in light emission from the exciton (denoted ‘X’ in Fig. 1a) and several charged exciton complexes which include the inter- and intra-valley trions (T1 and T2)^{30, 40, 41} as well as the negatively charged biexciton (XX⁻)²⁰⁻²². At low-energy photoexcitation, the intensity of these charged exciton complexes is weaker than the neutral exciton. In contrast, the high-energy photoexcitation enhances the emission intensity of all three charged exciton complexes (the trions and charged biexciton) relative to the exciton. This contrast between the photoluminescence spectra at the two different excitation energies (but the same excitation densities) reveals that the initial state of the photoexcitations significantly alters the distribution of emissive excitons, whereby a greater portion of charged exciton complexes can be achieved with higher-energy photoexcitation.

From the results in Figure 1, two lines of inquiry immediately surface. The first is to identify how the populations of emissive excitons evolve with increasing energy. The second is to determine if the increased excitation energy increases the brightness of the charged exciton complexes. This latter question equates to identifying whether or not the photoluminescence quantum yields of the states increase with energy. To quantitatively address these points, we use an excitation spectroscopy technique that precisely controls the excitation density and excitation area in our PL experiments for excitation energies from 1.80-2.66 eV. Precise control is required for several reasons. First, to meaningfully probe changes in the relative populations of exciton and

biexcitons, it is imperative that the photoluminescence spectra at different energies are acquired at the same excitation density. The relative fraction of biexcitons depends on the excitation density, giving rise to the super-linear power dependence shown in Figure 1b. By increasing the excitation density, the biexciton population will eventually overtake that of the exciton, and the photoluminescence spectrum will change from a regime where excitons dominate to one where charged biexcitons dominate. Further, at sufficiently large excitation density, the charged biexcitons saturate (see SI note 1), possibly limited by either the concentration of free carriers (e.g., doping), hot-phonons⁴², or the excitonic Mott transition⁴³. In addition to keeping the excitation density constant, a constant number of initial photoexcitations must also be maintained at each excitation energy to determine relative changes in the quantum yields and absolute brightness of the states.

Several experimental details and procedures need to be addressed to keep the above factors constant. The multilayer geometry of the sample induces strong modulation of the photoexcitation external quantum efficiency (EQE), which quantifies the fraction of incident photons on the sample that is absorbed by the 1L-WSe₂. Optical reflections at each interface in the hBN/1L-WSe₂/hBN/SiO₂/Si stack interfere with the incident light in the plane of the 1L-WSe₂ (see the cartoon inset in Fig. 1c)^{37 44} and result in a strong dependence of the photoexcitation EQE on the excitation energy. To account for this effect, we use transfer matrix method (TMM) calculations^{45, 46} for each photoexcitation energy. These calculations estimate the photoexcitation EQE given the geometry of the sample stack and the optical response of each material. Optical response functions reported in prior studies were used for the 1L-WSe₂ at 4 K⁴⁷, Si⁴⁸, SiO₂⁴⁹, and hBN⁵⁰. The results of the TMM simulations are shown in Figure 1c. The calculations capture the strong absorption

resonances associated with the excitons in the 1L-WSe₂ and a broadband envelope arising from interference effects that suppress the photoexcitation EQE at low and high excitation energies (see the SI note 2 for additional details). Using these TMM calculations, the excitation power of the laser at a given excitation energy can be calibrated such that the photon flux on the 1L-WSe₂ embedded in the dielectric stack can be precisely controlled.

Maintaining the same number of total excitations along with a constant excitation density for all excitation energies also requires maintaining a constant area of illumination. In the custom confocal microscope used here, chromatic aberrations can reduce the collimation of the beam entering the back aperture of the microscope objective, resulting in significant variations in the photoexcitation spot size. Even for perfectly collimated light, the diameter of a diffraction-limited laser spot depends on the wavelength of light, which varies from ~690–465 nm over the measurement range. To compensate for these variations, we implemented a Gaussian telescope before the microscope where the separation between the two lenses is set by a computer-controlled motorized stage. By adjusting the separation of the lenses and working with illumination areas that are $\sim 3\times$ larger than the diffraction limit, the area of the illumination is held constant in our measurements, as shown in Figure 1d. For all of the excitation energies, the average area of the photoexcitation spot size is $2.01\ \mu\text{m}^2$ which corresponds to a FWHM of $1.60\ \mu\text{m}$.

Energy-Dependent Quantum Yields of Trions and Charged Biexcitons

Figure 2a presents the results of the quantitative excitation measurement with constant excitation density and total number of excitations. The photoexcitation energy steps from 1.80–2.66 eV in 8.8 meV increments. The average excitation density (ρ_{exc}) at each energy is $\sim 3\times 10^{11}\ \text{cm}^{-2}$, equating to the generation of ~ 5000 excitations per laser pulse. Details on the calculation of the excitation

density can be found in the Methods section. Figure 2b shows three PL spectra taken at the photoexcitation energies of 1.83, 2.25, and 2.60 eV. The spectra are plotted on an absolute scale without any additional normalization or scaling. At 1.83 eV photoexcitation, the exciton dominates whereas at 2.25 eV and 2.60 eV, the charged biexciton dominates, confirming the observations in Figure 1. To resolve how the emission intensity depends on photoexcitation energy for a particular excitonic species, we integrate each PL spectrum around a small band centered on the respective emission feature (insets of Fig. 2c). The integrated intensities at each excitation energy for the exciton (top panel), the sum of the inter- and intra-valley trions (middle panel), and the charged biexciton (bottom panel) are shown in Figure 2c. A resonance at 1.875 eV appears in the excitation spectrum for each state, which as discussed in detail below, is suspected to be due to differences in the actual absorption spectrum of the 1L-WSe₂ used here and that reported in literature. In contrast to the exciton, a similar peak feature is superimposed on a step-like increase in the emission intensity at ~ 1.95 eV for the trions and the charged biexciton. This feature is absent in the excitation spectrum of the exciton.

The resonant feature at 1.875 eV that is present for all states raises suspicion that the excitation densities and initial number of photoexcitations for these energies are artificially high. Figure 3a compares the absorption spectrum of 1L-WSe₂ at 4 K reported in literature⁴⁷ (and used in the TMM calculations) to the reflectance contrast and linear photoluminescence excitation (PLE) spectrum of the hBN/1L-WSe₂/hBN/SiO₂/Si stack studied here. In contrast to the excitation spectroscopy of Figures 1 and 2, the linear PLE spectrum is acquired with a constant flux of photons on the 1L-WSe₂ at each excitation energy. As a result, the linear PLE measures relative changes of the product of the absorption and exciton quantum yield between different excitation

energies. With the interference effects fully accounted for by the above TMM model to assure a constant photon flux on the 1L-WSe₂, the PLE spectrum closely matches the absorption spectrum, with only small deviations that can be attributed to the different samples used. The A_{2S} and B_{1S} exciton resonances are observable in both spectra but are narrower in the PLE spectrum. At higher energies, the PLE spectrum increases following the same general trend of the absorption spectrum through the resonance of the C exciton (a full discussion of the features observed in the spectra can be found in SI note 3)⁵¹⁻⁵³. The similarity between the linear PLE and absorption spectra strongly implies that the quantum yield of the exciton does change with increasing energy, as was initially suspected from early PLE measurements^{38, 54}. Rather, our observation here, confirms prior linear PLE measurements of 1L-MoS₂ at 300 K³⁷, which made similar efforts to account for photonic interference effects.

In contrast to the linear PLE spectroscopy, the suspicious peak at 1.875 eV for the exciton state observed in Figure 2 suggests that there is a significant enhancement of its quantum yield at this energy. However, as discussed above, the linear PLE spectroscopy indicates that the quantum yield of the exciton does not depend on excitation energy. Further, no such peak or feature is observed in the exciton beyond these energies. Therefore, we strongly suspect that the excitation resonance at 1.875 eV for the exciton (Fig. 2c) is due to an under-estimation of the absorption strength of the A_{2S} exciton, resulting from a mismatch between the absorption spectrum of the sample and that reported in literature.

We rely on the published absorption spectrum because it was obtained by direct measurement, as opposed to the differential reflectance spectroscopy and Kramers-Kronig analysis that is required for our sample. The uncertainty in the latter analysis is greater than the uncertainty

associated with using the published spectra, where variations in material quality, doping, or strain will result in differences in energies and linewidths of the excitonic resonances. To correct for these discrepancies given the results of the linear PLE measurements, we scale the intensity of the exciton at each excitation energy such that its emission intensity is constant over the range of excitation energies, which is equivalent to assuming the exciton quantum yield does not change with excitation energy. The excitation spectra of the trions and charged biexciton are subsequently scaled by the same correction factor, taking into account the measured power-law at each excitation energy (c.f. Figure 1b). Figure 3b contrasts the resulting corrected excitation spectra with the raw data reported in Figure 2c.

The corrected spectra shown in Figure 3b report the relative changes in the quantum yield of each state with increasing excitation energy. In these spectra, the peak-like features in the excitation spectra of all of the states are completely removed, and the step-like feature that marks an onset of increased quantum yield is resolved for the charged exciton complexes. Given the analysis and considerations above, we assert that the corrected spectra in Figure 3b reflect the true energy-dependence of exciton, trion, and charged biexciton quantum yields from the initial photogenerated state in the 1L-WSe₂, revealing that maximal generation of trions and charged biexcitons (at the excitation density described above) are achieved by 2.2 eV, reaching maximum enhancements of 4× for the trions and 12× for the charged biexciton.

Scaling of Enhancement with Excitation Density and the Potential Role of Hot Free Carriers

From the results of the excitation spectroscopy above, maximally generating charged biexcitons requires excitation energies greater than the optical bandgap as well as large excitation densities. To explore the interplay of excitation density and the excitation energy-dependent quantum yield,

we investigated the power dependence of the enhancement at excitation densities spanning from $\sim 10^{10} \text{ cm}^{-2}$ to $\sim 10^{12} \text{ cm}^{-2}$ (nearly two orders of magnitude) with the same illumination FWHM of $1.60 \text{ } \mu\text{m}$. The power-dependent excitation spectra for each state are shown in Figure 4a. Each spectrum is scaled such that the emission intensity at the lowest excitation energies is unity, enabling the power-dependent progression of the enhancement (for the charged states) to be resolved. Since the enhancement is resolvable in the raw data and the correction process does not alter the observed trends, the reported spectra here are uncorrected. The strength of the enhancement for the trions and charged biexcitons increases (sub-linearly) with increasing excitation density, but appears to saturate at $\sim 3 \times 10^{11} \text{ cm}^{-2}$ and then decrease at higher densities. We note that the increase in the enhancement followed by a saturation with increasing excitation density is reminiscent of the PL intensity of defect states which saturates due to the finite number of emitters. This observation is discussed in more detail below.

The excitation spectra of the exciton show a subtle dependence on excitation power (Figure 4a), which is indicative of potential nonlinear behavior in the generation of exciton states. The combined excitation-density and excitation-energy dependent studies confirm this nonlinearity and its onset with increasing photoexcitation energy. Figure 4b compares how the exciton photoluminescence intensity scales with excitation density at photoexcitation of 1.80 eV and 2.40 eV . The functional relationship between the photoluminescence intensity (I) and excitation density (ρ_{exc}) is $I = I_0 \times \rho_{exc}^\alpha$, where I_0 is a constant of proportionality and α is the power of the scaling. As evident in the raw data as well as the power-law fit in Figure 4b, it is clear that the higher-excitation energy results in a super-linear scaling of the emission intensity of the exciton. To resolve how this transition develops with excitation energy, the value of α is determined (by

fitting) at each excitation energy (see SI note 4 for details). As shown in Figure 4c, the transition from linear scaling ($\alpha \leq 1.05 \pm 0.03$) to superlinear scaling ($\alpha \approx 1.14 \pm 0.03$) develops following a step-like progression at ~ 1.95 eV.

The increase in the exciton power law with increasing excitation matches the evolution of the quantum yields of the inter- and intra-valley trions and charged biexcitons reported in Figure 2. The scaling of the exciton power law saturates at $\alpha \approx 1.14$ at excitation energies beyond 2 eV, which is in good agreement with the energy of the quasiparticle band gap (2.0 eV, see SI note 5 for details). It is also within 150 meV of where the enhancement of the quantum yields of the trions and charged biexciton saturate. Considering the noise in the quantum yield and power-law excitation spectra, the saturation points coincide with each other within the uncertainties of the data. Finally, there appears to be a fine structure where the exciton power law is suppressed back towards linear near the A_{2S} and B_{1S} absorption resonances. Improving the determination of the saturation point and resolving the apparent resonant fine structure within the energy dependence of the power law scaling necessitate future studies. In the following, we will focus on the implications of the increase in the power-law scaling with excitation energy in understanding the enhancement effect.

The linear scaling at low excitation energies is due to the direct photoexcitation of Rydberg excitons at the K-point. In this case, the data indicates that the formation rate of the A_{1S} state from other excitons in the A manifold is linear and efficient, likely due to the extremely fast intra-valley relaxation rates in 2D semiconductors²⁸. At higher excitation energies, photoexcitation initially populates the continuum states beyond the quasiparticle bandgap^{27, 28, 31, 32}. With increased energy, the photoexcitations are more likely to form free carriers because there is a greater probability that

the correlated motion of the photoexcited electrons and holes can be destroyed during thermalization^{32, 37, 39}. In this regime, the formation of excitons is a bimolecular process that scales as the product of the free electron and free hole densities⁵⁵, analogous to the bulk recombination in other semiconductors^{56, 57}. If the formation of excitons from free carriers is efficient, the power-law scaling is approximately linear. As the formation efficiency decreases, the observed power law will become increasingly super-linear (see SI note 6 for a basic model). The subtle increase in the power-law reported in Figure 4 indicates the transition between these formation regimes in the 1L-WSe₂. Additional evidence of the photogeneration of free carriers by high-energy photoexcitation is present in dual-color pump-probe reflectivity measurements (see SI note 7 for details) as well as in previous ultrafast spectroscopy results^{28, 32}. In sum, the power-dependent spectroscopy shows that the onset of enhanced formation of the trions and charged biexciton coincides with photoexcitation above the quasiparticle bandgap, which marks the photogeneration of free carriers in the form of an electron-hole gas.

The power-law excitation spectra of the inter- and intra-valley trions and charged biexciton are reported in SI note 8. Following a similar trend, the power-law of the charged biexciton is enhanced from $\alpha \approx 1.65$ to $\alpha \approx 1.90$ while the power-law of the trions is enhanced from $\alpha \approx 1.20$ to $\alpha \approx 1.32$. An unambiguous interpretation of the enhanced power-law scaling of trions and charged biexcitons motivate future studies that utilize time-resolved techniques. At this point, we simply note that the transitions may indicate an optically induced increase in the free electron density or efficient super-quadratic formation from the free carrier population. We briefly elaborate on these potential hypotheses in the discussion section below.

Temperature Dependence of the Enhancement Effect

Finally, Figure 5 presents the temperature dependence of the enhancement of the quantum yields. The photoluminescence was measured at low- and high-energy photoexcitation (1.88 eV and 2.36 eV, respectively) at an excitation density of 10^{11} cm^{-2} at temperatures from 4-80 K. In this dataset, the FWHM sizes of the illumination areas are $1.04 \text{ }\mu\text{m}$ for 1.88 eV and $0.84 \text{ }\mu\text{m}$ for 2.36 eV. To account for the resulting differences in total excitations, the PL spectra in Figures 5a and 5b are scaled by the intensity of the exciton at 4 K (at the respective excitation energies). This approach uses the exciton at 4 K as a standard candle. For a single excitation energy, the scaling simultaneously highlights how the relative intensities of the states evolve with temperature. Comparing the two excitation energies, the scaling additionally resolves the (temperature-dependent) change in quantum yield, following the protocol established in Figures 2 and 3. By comparing the scaled intensities of the charged biexcitons at the two excitation energies, the quantum yield enhancement persists to 80 K but with significantly diminished magnitude than at 4 K. With decreasing temperature from 80 K, the scaled intensity of the charged biexciton increases at $\sim 40 \text{ K}$ at the higher excitation energy but not the lower excitation energy.

To summarize the temperature-dependence of the enhancement of the quantum yields, enhancement factors for the trions and charged biexcitons are calculated at each temperature from the ratio of the intensity under photoexcitation at 2.36 eV to that under photoexcitation at 1.88 eV. For instance, the enhancement factor for the charged biexciton at each temperature is given by,

$$\Gamma_{XX-} = \frac{I_{2.36 \text{ eV}}^{XX-} / I_{2.36 \text{ eV}}^{X,T=4 \text{ K}}}{I_{1.88 \text{ eV}}^{XX-} / I_{1.88 \text{ eV}}^{X,T=4 \text{ K}}}$$

The temperature dependence of Γ_{trions} and $\Gamma_{\text{XX-}}$ is shown in Figure 5c. The enhancement factors for both states sharply decrease as the temperature exceeds 10 K and converge to unity at higher temperatures. We note that above 80 K, emission from the charged excitons and biexcitons is suppressed, prohibiting measuring enhancement factors at higher temperatures. To quantify this behavior, the temperature dependence for each state is fitted to a modified Arrhenius model given by,

$$\Gamma = \frac{\Gamma_0}{1 + (\Gamma_0 - 1) \times \exp(-E_a/k_b T)}$$

Here, Γ_0 is the enhancement factor at 0 K, E_a is the characteristic activation energy of the enhancement, and k_b is the Boltzmann constant. The amplitude of the exponential term in the denominator is chosen to ensure that the enhancement factor converges to unity at elevated temperature. The modified Arrhenius model quantitatively captures the temperature dependence of the enhancement effect (see Figure 5c) and yields an activation energy of 6.5 meV (~ 75 K) for both the inter- and intra-valley trions and charged biexciton.

We note that a careful comparison of the enhancement factors at 4 K reveals suppressed enhancement as compared to Figures 1 and 2. These measurements were conducted before the other excitation spectroscopies discussed earlier in the paper. The charge state of the sample changed between the measurements, likely due to sample aging. For the temperature-dependent measurements here, the spectral evidence indicates that the sample is less n-doped than during the other measurements, reducing the intensity of the charged trions and biexciton by a factor of $\sim 1/4$. Despite this change, the sample exhibits the same qualitative dependence on excitation energy as reported in Figures 1 and 2.

Discussion

The work here demonstrates that the quantum yields of trions and charged biexcitons are enhanced with excitation above the quasiparticle band gap in 1L-WSe₂. To the best of our knowledge, this effect has not been previously reported in any system nor treated in any established theoretical model. From the data here, we can begin to narrow down the possible underlying mechanism of the enhancement. From excited state dynamics reported in SI note 9, the higher quantum yield of the charged biexciton does not correspond to a change in its excited state lifetime, further corroborating that the enhancement manifests in the ultra-fast formation dynamics of exciton complexes. From the temperature dependence, the measured activation energy of the enhancement is sufficiently smaller than the binding energies of the exciton complexes (15 meV – 30 meV)^{19-22, 58} and the dark-bright exciton fine structure splitting at the K-point (30 meV)^{5, 13, 14, 16, 40}, which excludes significant contributions from the dissociation of excitons or the temperature-induced brightening of K-point dark excitons. Further, this activation energy equates to a temperature of 75 K, which exceeds the critical temperatures of correlated ground states, such as Wigner crystallization in 1L-MoSe₂⁵⁹. In contrast, the activation energy is closer to the predicted energetic splitting between the momentum-dark KQ exciton and spin-bright KK exciton (≈ 6 meV)⁶⁰ and the binding energies of localized excitons in TMD semiconductors (10 – 100s meV)^{61, 62}.

Given that the enhancement is observed in the charged complexes, photo-induced changes in the carrier density of the 1L-WSe₂ could also play an important role. Previous experiments have established that the formation of charged excitons and charged biexcitons depends on the static background charge density¹⁹⁻²¹ and that photodoping can arise from the photoionization of color centers in the supporting hBN crystallites⁶³. To control for the possibility that our sample

accumulates a static charge during the measurements, we modulated the photoexcitation between 1.82 and 2.36 eV. These controls show that the absolute intensities of the states are highly repeatable over multiple cycles of the excitation energy (see SI note 10), excluding any quasi-persistent charging of the sample.

Consequently, based on prior studies, our current data, and our analysis, we identify two possible mechanisms that underlie the enhancement. The first mechanism begins with the enhanced formation of KQ excitons at high-energy photoexcitation, which is consistent with recent time- and angle-resolved photoemission spectroscopy measurements³⁵. The subsequent capture of the constituent K-point holes by defects could leave the remaining electron available to contribute to the formation of charged exciton complexes. The second alternative mechanism is that the direct formation of excitonic states from the photogenerated free carrier gas favors the formation of trions and charged biexcitons. Detailed consideration of rate models that describe the formation of exciton complexes from a free carrier gas predicts signatures of this mechanism that could be found in the power-law scalings of the states at large excitation densities. Such analysis and further experiments are beyond the scope of this work, and deconvolving the contributions of these two mechanisms motivates future studies at higher excitation densities (ideally up to the excitonic Mott transition), and possibly utilizing a direct correlation to more advanced spectroscopies such as time-resolved ARPES³⁵.

In light of the spectroscopy presented here, an open question in 1L-WSe₂ remains as to whether or not the formation of KQ excitons at large photoexcitation energies³⁵ significantly affects the PL quantum yield of the K-point excitons. Our spectroscopy (Figure 2) suggests that the suppression of photoluminescence due to nonradiative recombination of KQ excitons is

negligible at the moderate excitation densities and excitation energies probed here. To resolve this issue unequivocally, the accuracy of the photoexcitation EQE calibration needs to be improved, especially near the A_{2S} absorption resonance and for fully encapsulated samples at 4 K. An accurate dielectric function for the 1L-WSe₂ under these conditions is essential here (as well as in other quantitative experiments), necessitating improvement of Kramers-Kronig analysis of reflectance contrast spectra that significantly reduces the uncertainty in the calculated spectra.

In conclusion, we have shown that the initial condition of a photogenerated excited state substantially affects the photoluminescence quantum yields of the trion and charged biexcitons in 1L-WSe₂. Photoexcitation at energies above the quasiparticle bandgap enhances the quantum yields by factors up to 4 $\times$ and 12 $\times$ for the trions and charged biexcitons, respectively. To the best of our knowledge, such enhancements have not been previously reported, making the effect presently unique to 1L-WSe₂ and potentially other TMD semiconductors. Observation of the enhancement is enabled by meticulous excitation spectroscopy that uses electromagnetic modeling and precise control of the illumination area to maintain constant excitation density and the total number of generated excitations over a broadband range of excitation energies. As a result, relative changes in the quantum yield with excitation energy can be probed for both linear excitations (excitons and trions) as well as nonlinear excitations (biexcitons and charged biexcitons). Analysis of the evolution of the enhancement with increasing excitation energy and temperature provides insight into the underlying mechanism, excluding several processes. Potential contributions are possible from the formation of momentum-dark excitons, electron/hole capture by defects, and favored formation of charged exciton complexes from an electron-hole gas. Deconvolving their respective roles motivates future studies that implement the excitation spectroscopy here in

conjunction with state-of-the-art ultrafast techniques^{11, 28, 32, 35, 36}. The quantum yield enhancement highlights how the complexity of excited state thermalization and exciton formation in 2D materials at low temperatures can be utilized to tailor the resulting sub-populations of excitons responsible for light emission and other optoelectronic processes. Under pulsed excitation, this tunability can be used for deeper investigations of out-of-equilibrium dynamics under intense coulombic interactions whereas, under steady-state excitation, these results provide insight into how to maximize the yields of exciton complexes for low-temperature optoelectronic and quantum applications. In particular, future studies should focus on how these effects manifest for neutral biexcitons and localized biexciton states²³.

Methods

Sample Fabrication

The fully encapsulated hBN/1L-WSe₂/hBN sample was assembled by aligning the constituent crystallites on a polymer stamp and transferring them to the target Si/SiO₂ substrate using a flip-chip technique⁶⁴. 1L-WSe₂ and thin hBN crystallites were mechanically exfoliated using a scotch tape method. Each layer of the heterostructure stack was then sequentially picked up in bottom-up order by a polymer stamp (PPC + PDMS) before flipping the stack onto the supporting Si/SiO₂ substrate. The sample was subsequently vacuum annealed to remove the underlying PPC polymer after assembly.

Cryogenic Photoluminescence Spectroscopy

Cryogenic photoluminescence measurements were conducted by cooling the sample in a closed-cycle liquid helium cryostat with optical access (Montana Instrument s50 Cryostation). The sample

was illuminated with pulsed laser light generated from a supercontinuum fiber laser (NKT photonics SuperK EXTREME, pulse width = 55 ps, rep. rate = 78 MHz) that was filtered with an acoustic-optic tunable filter (Gooch and Housego, filter bandwidth ≈ 4 nm). Light was focused onto the samples using a Nikon 40 $\times$ objective (NA = 0.6) with tunable correction for spherical aberration. Luminescence was collected in a back-scattered geometry and directed to a Czerny-Turner optical spectrometer (Horiba iHR320), dispersed with a mechanically ruled grating (groove density = 600 g/mm), and measured with a scientific CCD camera (Andor iDus 416, cooled to -55 °C) after laser light was rejected with a series of interference filters. Precise positioning of the laser on the sample was achieved by scanning the beam over the sample using a 4f-imaging system in conjunction with a 2-axis galvanometric scan mirror.

Calibration of the Illumination Area for Quantitative Photoluminescence Excitation Spectroscopy

A Gaussian telescope was used to tailor the collimation of the laser in order to maintain a constant area of illumination for all excitation energies. To find the precise configuration of the Gaussian telescope, the illumination profile was monitored as the separation of the lenses and the laser wavelength was changed. Images of the focused laser spot on the sample were taken on a grid of laser colors and lens separations and each image was fitted with a 2D Gaussian intensity profile. The spot area for the excitation spectroscopy was calculated by finding the area of the ellipse defined by the variance along the semi-major and semi-minor axes of the optimized 2D Gaussian. We then selected the smallest target illumination area that our system was able to maintain across the extent of the excitation energies probed (1.80 eV – 2.68 eV) which had an area of $\approx 1.47 \mu\text{m}^2$ (as defined by the variances of the 2D Gaussian) for our experiments. We estimate that the

uncertainty in the spot area is +/- 3.3% due to the coarseness between points in the laser color/lens separation grid used to generate the calibration curve.

Definition of the Excited State Density

In our experiments, we define the excited state density as

$$\rho_{exc} = \frac{(P[J/s]) \times (6.242 \times 10^{18}[eV/J]) \times (EQE)}{(78 \times 10^6[pulses/s]) \times (E_{exc}[eV]) \times (A[cm^2])}$$

Where P is the time-averaged power delivered to the sample by the incident laser, $6.242 \times 10^{18}[eV/J]$ is the conversion from Joules to eV, EQE is the photoexcitation external quantum efficiency, $78 \times 10^6[pulses/s]$ is the repetition rate of the laser, E_{exc} is the excitation energy in eV, and A is the characteristic illumination area. We note that this definition reports the excitation density integrated throughout each laser pulse (55 ps, FWHM), and that the instantaneous excitation density will depend on the dynamics of the photoexcitations.

Linear Photoluminescence Excitation Spectroscopy

To perform the standard linear PLE measurement, the laser power at each excitation energy was calibrated to maintain a constant photon flux through the monolayer while accounting for thin-film interference effects using the TMM model.

Reflectance Contrast Spectroscopy

The reflectance contrast was measured by imaging a back-illuminated pinhole onto the sample and calculating the normalized difference of the reflectance spectrum in regions consisting of hBN/1L-WSe₂/hBN/SiO₂/Si versus hBN/SiO₂/Si. The reflectance contrast is defined as,

$$RC = \frac{R_{off} - R_{on}}{R_{on} + R_{off}}$$

where R_{on} is the reflection from the regions that include 1L-WSe₂.

Data availability: The authors declare that all data supporting the findings of this work are available from the corresponding authors upon reasonable request.

Code availability: The authors declare that all analysis code supporting the findings of this work are available from the corresponding authors upon reasonable request.

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Competing interests: The authors declare no competing interests.

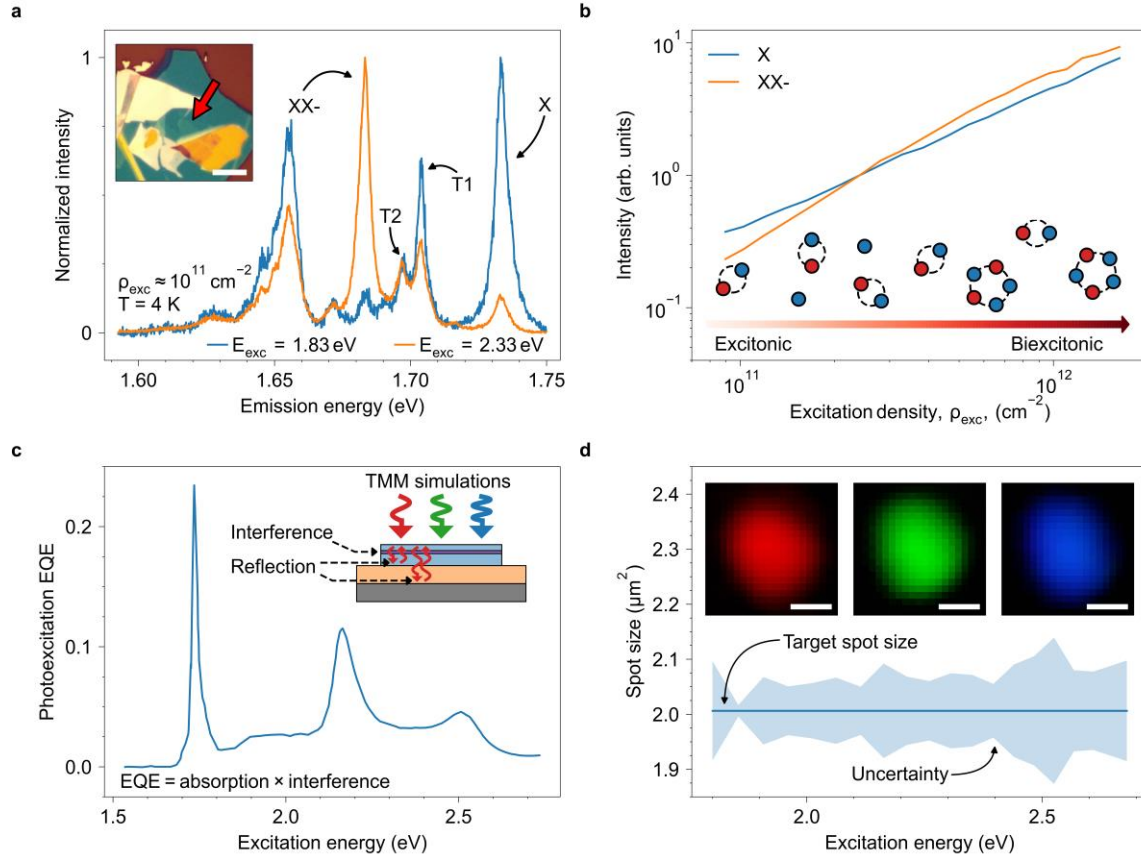


Figure 1 – Enhanced relative emission of trions and charged biexcitons with high-energy photoexcitation and the factors that influence emission intensities of linear and nonlinear states in 2D heterostructures. (a) Photoluminescence spectra of the 1L-WSe₂ sample that is fully encapsulated in hBN (optical micrograph inset, scalebar: 10 μm) after optical excitation with low energy light, $E_{\text{exc}} = 1.83$ eV (blue), and high energy light, $E_{\text{exc}} = 2.33$ eV (orange). (b) Excitation density-dependent photoluminescence spectroscopy of the exciton (X, blue) and charged biexciton (XX-, orange). (c) The energy dependence of the photoexcitation external quantum efficiency (EQE), which accounts for 1L-WSe₂ absorption at $T = 4$ K and interference arising from the photonic cavity created by the underlying hBN/SiO₂/Si interfaces. (d) Experimental control of the area of illumination (i.e., spot size) for each excitation energy as detailed in the main text. The target spot size is indicated by the solid line and the estimated uncertainty is shown by the shaded region. Inset are optical images of the focused laser spot on the sample while using red, green, and blue laser excitation energies. All scalebars: 1 μm .

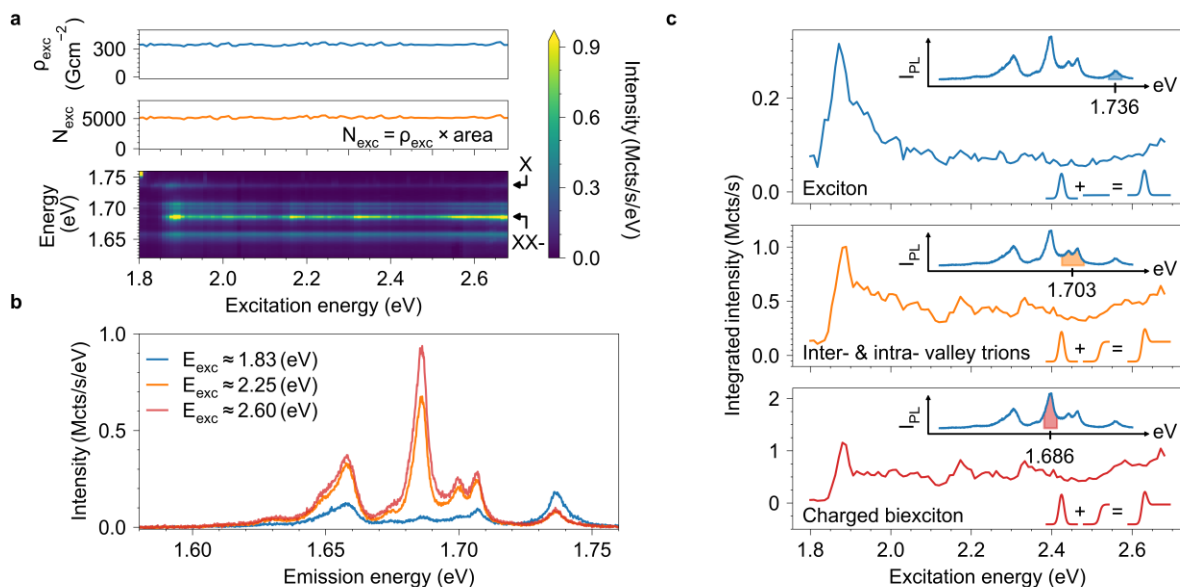


Figure 2 - Enhancement of the absolute intensity of trions and charged biexcitons with increased excitation energy. (a) Bottom panel, the photoluminescence spectra acquired at 100 excitation energies (E_{exc}) spanning from 1.80 - 2.66 eV. For all energies, the excitation density (ρ_{exc} , top panel) and total number of excitations (N_{exc} , middle panel) are held constant. (b) Photoluminescence spectra taken from representative excitation energies from (a). (c) The excitation spectrum of the exciton (top panel), inter- and intra- valley trions (middle panel), and charged biexciton (bottom panel), extracted from the data in the bottom panel of (a). Upper insets: example photoluminescence spectra with the integration band used to calculate the excitation spectrum denoted by the colored overlay. Bottom insets: a schematic that deconvolves the broadband trend from the suspected artifact at 1.875 eV.

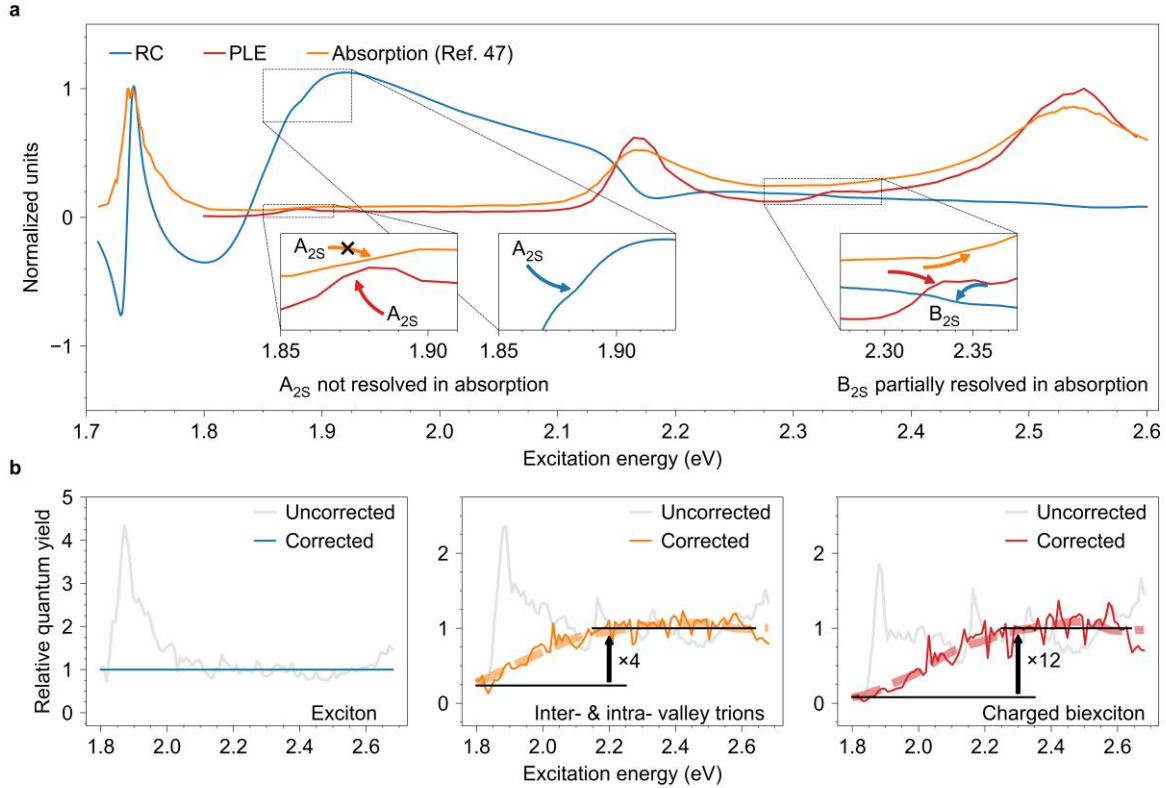


Figure 3 – Determination of the energy-dependent quantum yields of the neutral exciton, trion, and charged biexciton in 1L-WSe₂. (a) Comparison of the measured reflectance contrast (RC, blue) and standard linear photoluminescence excitation spectroscopy (PLE, red) measured at 4 K from the sample studies with the absorption spectrum reported in ref. [47] (orange) and used in the calibration of the photoexcitation external quantum efficiency. (b) The relative changes of the quantum yields for the exciton, inter- and intra- valley trions, and charged biexciton derived by correcting the exciton quantum yield to be constant with excitation energy. Corrected spectra are shown in color with a moving average of the corrected signal shown by the dashed lines. The uncorrected data is underlaid in grey.

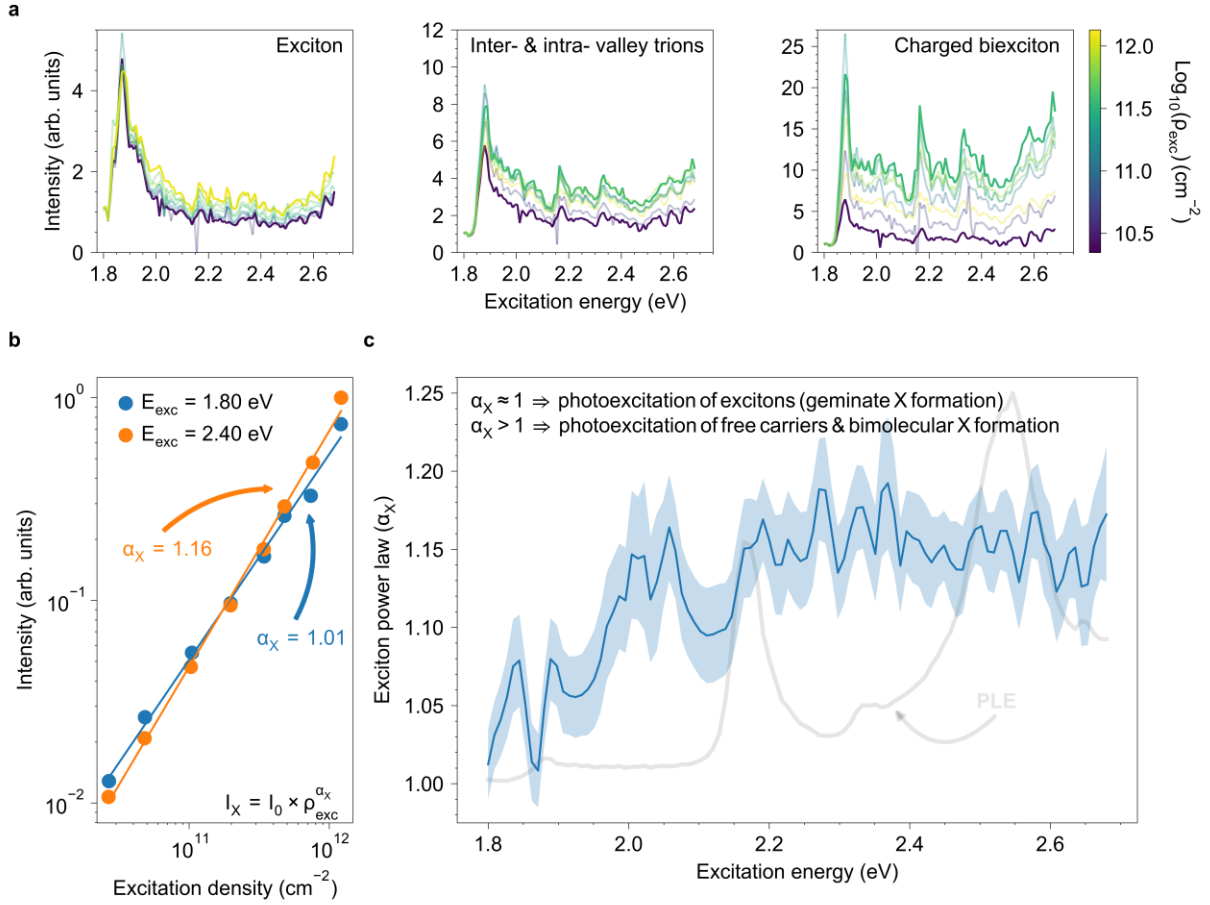


Figure 4 – Power dependence of the quantum yield enhancement and its correlation with exciton formation from free carriers. (a) Excitation spectra of the exciton, inter- and intra- valley trions, and charged biexcitons taken at excitation densities (ρ_{exc}) spanning $\rho_{\text{exc}} \approx 10^{10} \text{ cm}^{-2}$ - $\rho_{\text{exc}} \approx 10^{12} \text{ cm}^{-2}$. Each spectrum is scaled to its average at $E_{\text{exc}} < 1.83 \text{ eV}$. (b) Power-dependent photoluminescence spectroscopy of the exciton conducted with low- ($E_{\text{exc}} = 1.80 \text{ eV}$, blue) and high- ($E_{\text{exc}} = 2.40 \text{ eV}$, orange) excitation energy. Each trend is fit to extract the characteristic power-law. (c) The excitation spectrum of the exciton power law (α_X , solid) and estimated uncertainty (shaded). The photoluminescence excitation (PLE) spectrum measured at 4 K is underlaid for comparison to the variations in α_X .

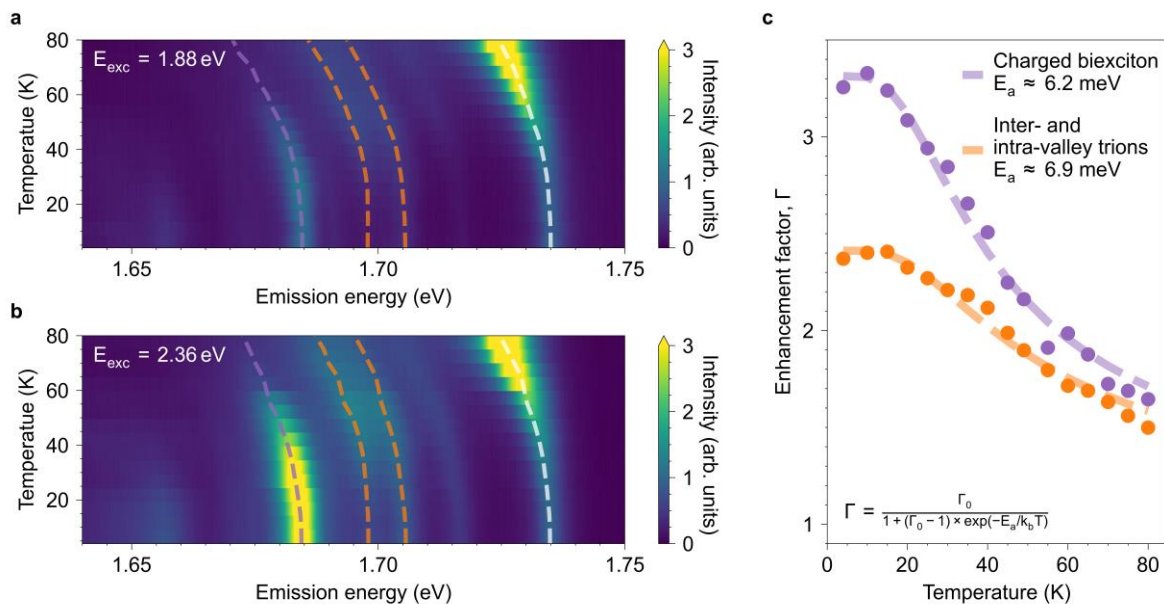


Figure 5 - Temperature dependence of the quantum yield enhancement of trions and charged biexcitons. (a), (b) Temperature-dependent photoluminescence at excitation energies of 1.88 eV and 2.36 eV, respectively. The excitation density is held constant at 10^{11} cm^{-2} . The spectrum at each temperature is scaled to the intensity of the exciton at 4 K to account for the difference in spot sizes at the two different excitation energies. (c) The temperature dependence of the enhancement factor for the charged biexciton (purple, scatter) and trions (orange, scatter). Fits to the data using a modified Arrhenius model are shown by the colored dashed lines.

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Supplementary Information: Increase of Trion and Charged Biexciton Photoluminescence
Quantum Yields by Above-Gap Excitation in Single-Layer WSe₂

Supplementary Note 1: Saturation Behavior of the Charged
Biexciton at Elevated Excitation Densities.

Figure S1 presents additional power-dependent measurements that further establish that the formation of the charged biexciton is enhanced by using high-energy photoexcitation. In these measurements, the power-dependent photoluminescence (PL) intensity of the charged biexciton relative to the PL intensity of the exciton is measured at an excitation energy of 1.99 and 2.33 eV. Critically, these measurements reveal that the saturation value of the relative intensity is increased at elevated excitation energy. This unambiguously establishes that more charged biexcitons are generated *relative to excitons* at elevated excitation energies, and that the relative enhancement cannot be attributed to a miscalibration in the excitation density. This result is robustly confirmed by an additional systematic study, which is summarized in Figure S1b, that tracks the maximum relative intensity of the charged biexciton with photoexcitation energies spanning 1.90 eV and 2.30 eV at a slightly elevated temperature, estimated to be approximately 20 – 30 K. The measurements shown in Figure S1 were conducted before the quantitative PLE measurements discussed in Figures 1-4 of the main text. The spectroscopic evidence (e.g., the relative PL intensity of the trions to exciton) indicates that the sample was less n-doped in the measurements presented in Figure S1 than in Figure 1-4 of the main text and that the overall magnitude of enhancement is reduced.

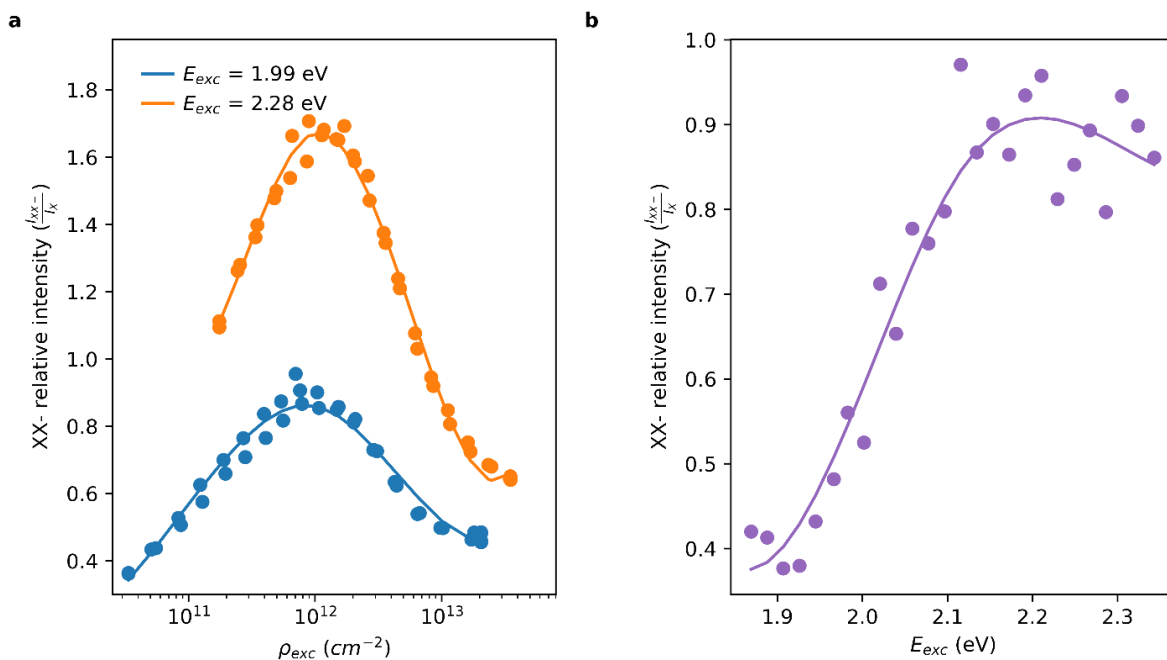


Figure S1 – Saturation of the charged biexciton PL emission as measured relative to the PL emission of the neutral exciton. a power-dependence of the relative intensity of XX- at a low and high excitation energy (1.99 and 2.28 eV, respectively) at 4 K. Critically, the maximum relative generation of XX- with low energy photoexcitation does not exceed the maximum with high energy photoexcitation. b The excitation spectrum of the maximum relative XX- intensity at a slightly elevated temperature ($T \approx 20 - 30$ K).

Supplementary Note 2: Transfer Matrix Method Simulations Used to Calibrate the Photoexcitation External Quantum Efficiency.

The calibration of the photoexcitation external quantum efficiency (EQE) relies on an estimate of the photonic cavity effects arising from thin-film interference due to the stratified stack of dielectric layers within our sample (hBN/1L-WSe₂/hBN/SiO₂/Si). Here, we leverage a numerical transfer matrix method implemented in Python^{2,3} to find full solutions to Maxwell's equations for a simplified model of the sample under monochromatic coherent laser illumination. The geometry of the sample is approximated as semi-infinite dielectric layers with the true thicknesses of the physical stack (hBN layers; < 1 nm top and 23 nm bottom, as measured by atomic force

microscopy, 1L-WSe₂; assumed to be ≈ 0.7 nm, SiO₂; grown to ≈ 285 nm as reported by the wafer supplier, Si; modeled as infinitely extending below the stack). The laser illumination is approximated as a plane wave that is incident normal to the stack with in-plane polarization. We also use the full complex dielectric function of each material, as reported by the references provided in the main text. The 1L-WSe₂ absorption spectrum was shifted slightly to align the B exciton resonance with that in the linear PLE spectrum of the sample. The simulation provides a

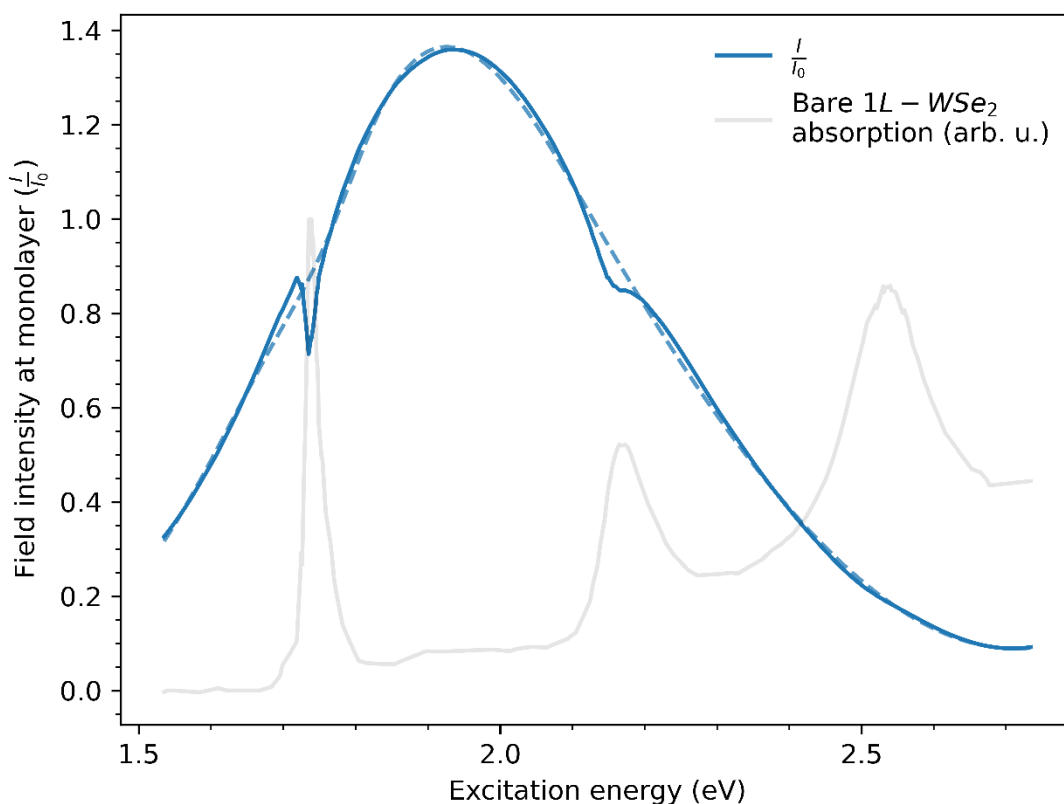


Figure S2 – Calculated photonic cavity resonance of the hBN/1L-WSe₂/hBN/SiO₂/Si dielectric stack. The field intensity relative to the intensity of the incident plane wave at the 1L-WSe₂ is shown by the solid blue line. Smoothing by spline interpolation is done to remove the sharp discontinuities caused by the strong absorption resonances in the 1L-WSe₂ and is shown by the blue dashed line. Underlaid in grey is the absorption spectrum of the bare 1L-WSe₂ reported by ref1.

quantitative estimate of the optical absorption in each layer of the stack for a given excitation energy, from which we isolate the absorption in the 1L-WSe₂ layer to calibrate the photoexcitation EQE. Finally, to find the excitation energy dependence of photoexcitation EQE, we run the simulation repeatedly for different excitation energies by tuning the wavelength of the plane-wave illumination across the desired measurement window.

The variation in the field intensity in the plane of the 1L-WSe₂ with excitation energy is shown in Figure S2, more directly illustrating the photonic cavity effects that modulate the 1L-WSe₂ absorption spectrum.

Supplementary Note 3: Discussion of the Low-Energy Resonance in the Excitation spectra

The absorption spectrum for 1L-WSe₂ used in the TMM calculations was taken from a prior study¹. It was not directly measured for this sample. To assess such possible discrepancies, the reflectance contrast⁴ and standard photoluminescence excitation (PLE)⁵⁻⁷ spectra of our sample are reported in Figure 3a of the main text. Combined, these spectra allow us to identify the absorption resonances of the excitonic species in our encapsulated sample at $T = 4$ K and qualitatively compare their energies, relative intensities, and linewidths to the absorption spectrum used.

The spectra contain the expected features of interband transitions and Rydberg-like resonances of the multiple manifolds of excitons^{8,9}. The lowest energy optical transition at 1.74 eV arises from the A_{1S} state of the lowest-energy K-point exciton. At 1.875 eV, a much weaker transition is observed in the measured reflectance contrast and PLE spectra. This feature is associated with the A_{2S} state of the lowest-energy K-point exciton. This feature, however, is not well-resolved in the published absorption spectrum that was used for the photoexcitation EQE

calibration. Beyond the A_{2S} transition, the energy of the quasiparticle bandgap (i.e., the lowest-energy interband transition) is estimated to be ~ 2.0 eV in our encapsulated sample (see SI for details of the estimate)¹⁰, but a clear corresponding feature is not identifiable in any of the spectra as expected^{5, 11}. Additional features at higher energies are attributed to the Rydberg states of the higher-energy K-point exciton where the hole exists in the lower spin-split valence band (i.e., the B_{1S} and B_{2S} excitons), and the C resonance¹². All of these higher-energy features are observed in the spectra of Figure 3 in the main text, with the exception that the B_{2S} transition is partially obscured in the absorption spectrum. Finally, the excitonic transitions are superimposed on a broadband background of continuum transitions that slowly increase in strength with increasing energy, which is consistent with previous reports^{1, 4, 7, 11}.

Given that the signatures of the A_{2S} absorption resonance appear in the reflectance contrast and PLE spectra, but not the absorption spectrum used to calibrate the photoexcitation EQE, we conclude that the peak at 1.875 eV in the excitation spectra is additional absorption by the Rydberg exciton that the PEQE calibration does not account for.

Supplementary Note 4: Procedure to Estimate the Uncertainty of the Power-Law Fitting.

The power-law scaling relationship was extracted from the power-dependent photoluminescence presented in Fig. 4a of the main text. The power-dependent PL at each excitation energy was fitted with the power-law scaling relationship described in the main text. Non-linear least squares regression was done to fit the logarithm of the data to the logarithm of the objective function, which more evenly weights the residuals at low excitation densities with that at high excitation densities.

To produce an estimate of the uncertainty in the fitting, all 120 possible combinations of 7 data points were fit to construct a statistical ensemble of the fitted power-law scaling relationships at each excitation energy. The mean and standard deviation of this ensemble are reported as the power law and associated uncertainty at each excitation energy.

Supplementary Note 5: Estimation of the Quasiparticle Bandgap Energy.

Using magneto-optical spectroscopy of the excitonic Rydberg states, ref. 13 developed a model describing how the binding energy of the 1S state of the A exciton depends on the average dielectric constant of the material surrounding the 1L-WSe₂. Following ref. 13, the dielectric constant of the bottom layer of hBN is $\epsilon_{bottom} = 4.5$. Because the top-layer of hBN is only 1 nm thick, we assume that the dielectric constant of the top layer is $\epsilon_{top} \approx 1$, corresponding to vacuum. Using these values, we calculate the average dielectric constant surrounding the 1L-WSe₂ to be $\kappa = \frac{1}{2}(\epsilon_{top} + \epsilon_{bottom}) \approx 2.8$. Applying this estimate of κ to the model in ref. 13 yields a predicted exciton binding energy of ~ 260 meV, placing the quasiparticle bandgap at ~ 2.0 eV. We note that the intrinsic carrier density will affect the exciton binding energy, resulting in an additional source of uncertainty in this estimate. However, both ref. 13 and our study use single-layers of 1L-WSe₂ that are mechanically exfoliated from as-grown bulk, so we estimate that both samples have similar carrier densities to make such a difference negligible.

Supplementary Note 6: Basic Model of Power-Law Suppression.

In the main text, we discuss the suppression of the exciton power law in the bimolecular formation regime towards a saturation value of approximately 1.15. Here, we use a simple model consisting

of two coupled sub-populations to investigate the suppression. The set of governing rate equations in the model is,

$$\begin{aligned} \frac{dn_1}{dt} &= I - k_{1 \rightarrow 2}(n_1)^p - k_{1 \rightarrow 0}(n_1)^q \\ \frac{dn_2}{dt} &= k_{1 \rightarrow 2}(n_1)^p - k_{2 \rightarrow 0}n_2 \end{aligned}$$

The population n_1 is pumped directly by a driving function, I , which controls the injection of excitations into the system. Subsequently, n_1 can either decay directly to the ground state (i.e., out of the interacting system of excitations) at a rate of $k_{1 \rightarrow 0}(n_1)^q$ or pump the second excited-state population, n_2 , at a rate of $k_{1 \rightarrow 2}(n_1)^p$. $k_{1 \rightarrow 2}$ and $k_{1 \rightarrow 0}$ are constants of proportionality and p and q are power laws.

We analyze this model by first calculating the probability that an excitation in the first population decays to the second:

$$P\{1 \rightarrow 2\} = \frac{k_{1 \rightarrow 2}(n_1)^p}{k_{1 \rightarrow 2}(n_1)^p + k_{1 \rightarrow 0}(n_1)^q}$$

Which is the ratio of the coupling rate from $1 \rightarrow 2$ to all rates that depopulate n_1 .

This simplifies to,

$$P\{1 \rightarrow 2\} = \frac{1}{1 + \frac{k_{1 \rightarrow 0}}{k_{1 \rightarrow 2}} n_1^{q-p}}$$

When the coupling to the second population is very fast as compared to relaxation to ground,

$$P\{1 \rightarrow 2\}_{efficient} \approx 1$$

When the coupling between the two populations is relatively slow,

$$P\{1 \rightarrow 2\}_{inefficient} \approx \frac{k_{1 \rightarrow 2}}{k_{1 \rightarrow 0}} n_1^{p-q}$$

Considering that the growth of n_1 is directly proportional to the driving function, I , the total population of n_2 will scale as,

$$n_{2,efficient} \approx I$$

$$n_{2,inefficient} \approx I^{1+p-q}$$

To model bimolecular exciton formation, we take I to be directly proportional to the intensity of the laser, n_1 to represent the density of the free carrier gas (i.e., the pair density of uncorrelated electrons and holes, $\sqrt{n_e n_h}$), and n_2 to represent the density of excitons. We set $p = 2$ so that the generation rate of the exciton population scales as the product of the electron and hole densities (i.e., bimolecularly), and $q = 1$ to represent a Shockley-Reid-Hall type of recombination channel for the free carrier gas. This yields,

$$n_{2,efficient} \approx I$$

$$n_{2,inefficient} \approx I^{1+2-1} = I^2$$

Demonstrating that the power-law scaling of an exciton sub-population can be tuned by the competing coupling rates within a model of interacting populations.

Supplementary Note 7: Additional Evidence for the Optical
Generation of Free Carriers by Dual-Color Transient
Reflection Spectroscopy.

We also find evidence of the optical generation of free carriers after high-energy photoexcitation in dual-color pump-probe reflectivity measurements conducted on a 1L-WSe₂ sample supported by an hBN crystallite at room temperature. The transient reflectivity measurements were performed on a custom-built pump-probe microscope with a convolved spatial resolution of 650 nm. Figure S3 shows the time-dependent change in the transient NIR reflectivity ($\lambda_{\text{probe}} = 800$ nm,

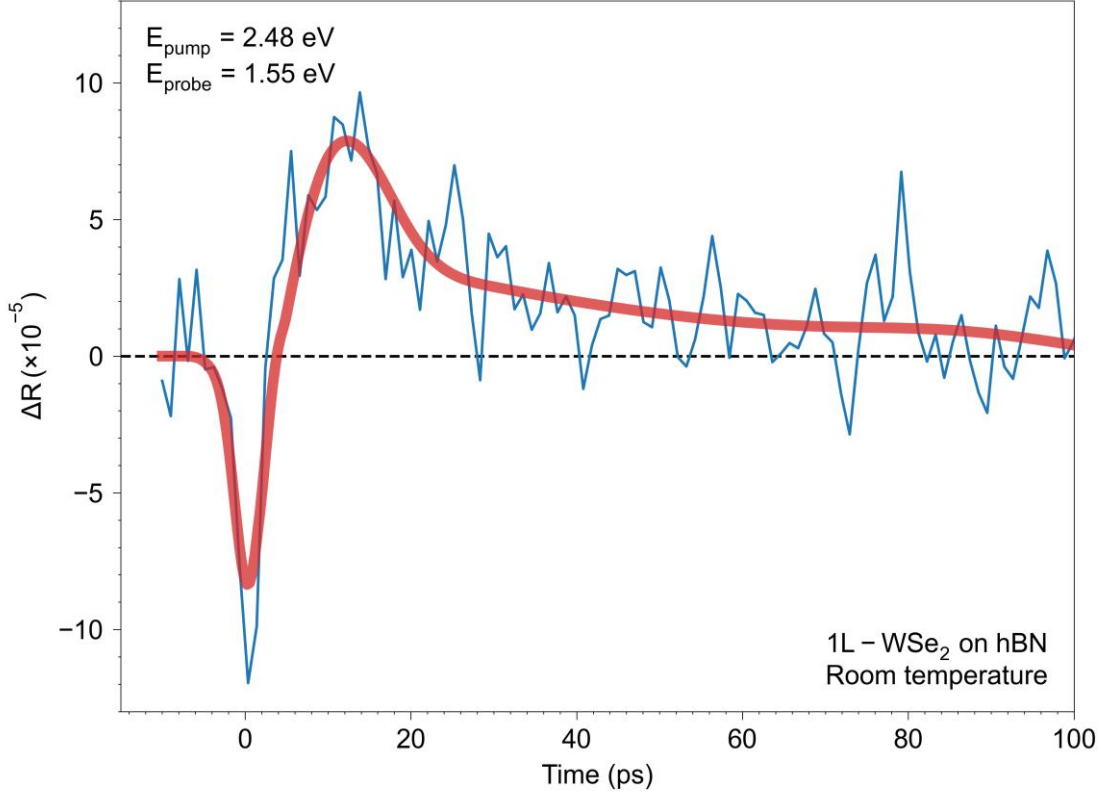


Figure S3 – Dual-color pump-probe transient reflectivity of a 1L-WSe₂/hBN sample at room temperature. The optical pump energy of 2.48 eV is well above the quasiparticle bandgap of the WSe₂ while the optical probe energy of 1.55 eV is on the very low-energy tail of the main exciton PL peak. Data is shown by the solid blue line and a smooth guide to the eye is shown by the transparent red line.

1.55 eV) after high-energy optical pumping ($E_{\text{exc}} = 2.48$ eV, pump power = 7.8 μW). At very short time delays, there is a rapid decrease in the reflectivity, consistent with the ultrafast optical response of a free carrier plasma¹⁴ that results in a reduction in the refractive index of 1L-WSe₂:

$$\Delta\epsilon = -\frac{n_{fc}e^2}{d\epsilon_0\mu} \times \frac{1}{\omega^2 + i\omega\Gamma}$$

Where n_{fc} is the free carrier pair density, d is the monolayer thickness, ϵ_0 is the permittivity of free space, μ is the reduced mass of electron-hole pairs, e is the electron charge, ω is the frequency

of the probe, and Γ^{-1} is the carrier scattering time. Assuming a carrier injection density of approximately 10^{12} cm^{-2} , a reduced mass of 0.17 times the free electron mass, a carrier scattering rate of 0.052 fs^{-1} , and a monolayer thickness of 0.7 nm,

$$\Delta\epsilon = -\frac{n_{fc}e^2}{d\epsilon_0\mu(\omega^2 + i\omega\Gamma)}$$

$$\approx -\frac{(10^{16}[\text{m}^{-2}])(2.5 \times 10^{-38}[\text{C}^2])}{(0.7 \times 10^{-9}[\text{m}])\left(8.8 \times 10^{-12}\left[\frac{\text{C}^2\text{s}^2}{\text{m}^3\text{kg}}\right]\right)(0.17 \times 9 \times 10^{-31}[\text{kg}])(5 \times 10^{30}[\text{s}^{-2}] + i2.2 \times 10^{15}[\text{s}^{-1}] \times 0.052 \times 10^{15}[\text{s}^{-1}])}$$

$$\Delta\epsilon \approx -5 \times 10^{-2} + i1 \times 10^{-3}$$

Without the optical pump, $\epsilon \approx 30$ for 1L-WSe₂. The expected change in reflectivity at an air/1L-WSe₂ interface with a perfectly matched layer supporting the 1L-WSe₂ is,

$$\Delta R = \left| \frac{\sqrt{30 - 5 \times 10^{-2} + i10^{-3}} - 1}{\sqrt{30 - 5 \times 10^{-2} + i10^{-3}} + 1} \right|^2 - \left| \frac{\sqrt{30} - 1}{\sqrt{30} + 1} \right|^2 \approx -3 \times 10^{-4}$$

When thin-film interference effects are accounted for by using a TMM simulation,

$$\Delta R \approx -6 \times 10^{-5}$$

This is in remarkable agreement with the magnitude of the negative ΔR signal observed at zero-time delay.

At longer time delays, the initial decrease in reflectivity disappears and a weak overall increase in the reflectivity is observed, which decays with a characteristic time of approximately 14 ps. We suspect that this subsequent increase in reflectivity is indicative of either a ground-state bleach in the low-energy Urbach tail of the room-temperature exciton, Coulomb renormalization, or heating.

We also attempted to measure the transient reflectivity after lower energy optical pumping $E_{\text{pump}} = 1.91 \text{ eV}$ (650 nm). However, we were unable to detect any change in the transient reflectivity up to a maximum pump power of approximately 5 μW . We attribute the null result

twofold; a relatively lower photoexcitation EQE at $E_{\text{pump}} = 1.91$ eV than at $E_{\text{pump}} = 2.48$ eV and reduced optical generation of free carriers by the lower energy pump. We speculate that a bleaching signal like that observed after higher-energy pumping was present yet undetectable by our experimental setup and that the free carrier response was simultaneously diminished.

These results lend evidence that free carriers are generated at elevated excitation energy in a 1L-WSe₂ sample supported by an hBN crystallite at room temperature. Differences concerning free carrier generation after lower-energy optical pumping remain inconclusive using this measurement technique.

Supplementary Note 8: Trion and Charged Biexciton Power Laws.

The excitation spectrum of the sum of the inter- and intra-valley trions and charged biexciton are shown in Figure S4. As discussed briefly in the main text, the power-laws for the exciton complexes increase with increasing E_{exc} , up to a saturation level at ≈ 2.1 eV.

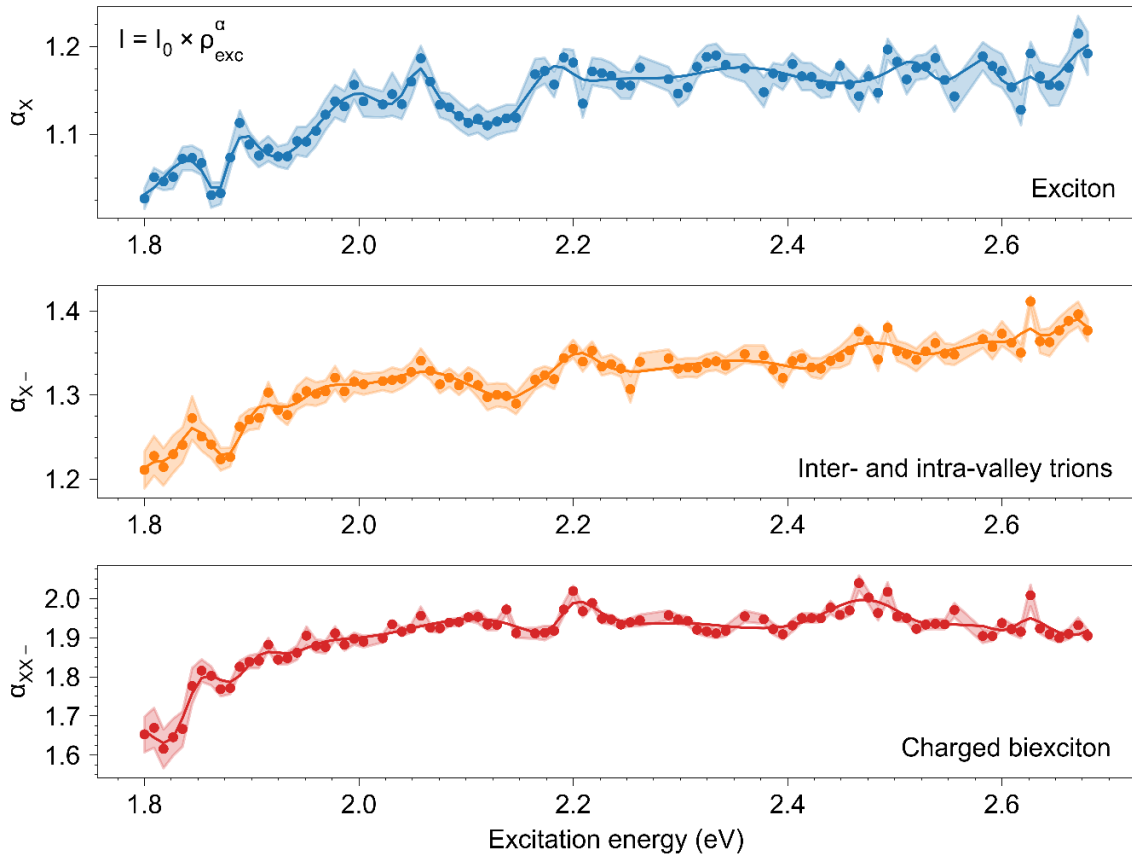


Figure S4 – Excitation spectra of the exciton, inter- and intra-valley trions, and charged biexciton power-law scaling with excitation density. Data is shown by the scatter, estimated uncertainty by the shaded region, and a smooth guide to the eye by the solid line.

Supplementary Note 9: Excitation Energy-Dependent Relaxation Dynamics of the Charged Biexciton.

To gain more insight into the dynamics of the enhancement of the charged biexciton, we investigated whether photoexcitation above the quasiparticle bandgap (QPBG) significantly alters the relaxation dynamics and effective lifetime of the charged biexciton from those when excited below the QPBG (potentially indicating an increase in Auger-type exciton-exciton interactions, for instance). Figure S6 shows the spectrally- and time-resolved PL of the charged biexciton in both excitation regimes at an average excited state density of 10^{11} cm^{-2} . For both excitation regimes, the

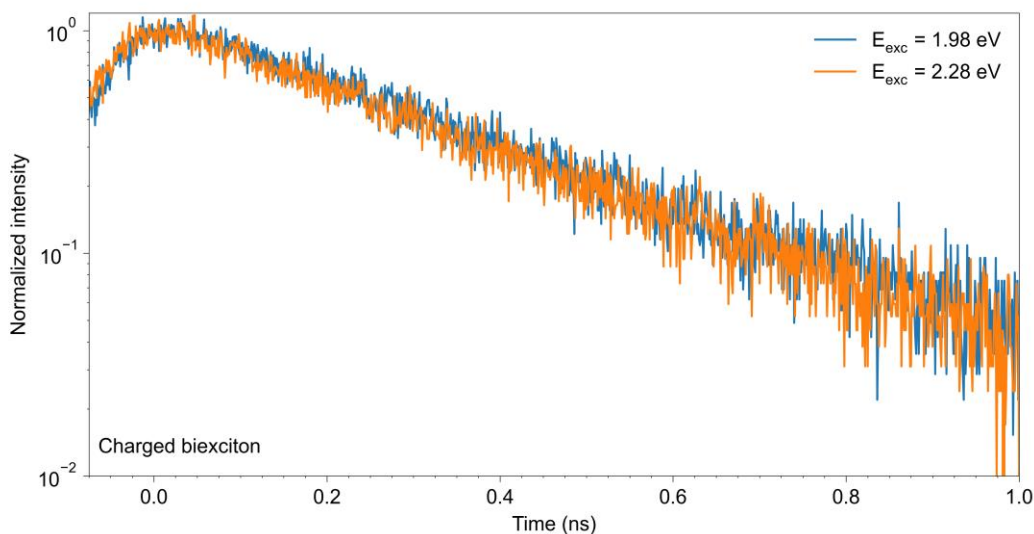


Figure S6 – Excited state relaxation dynamics of the charged biexciton with photoexcitation at 1.98 eV and 2.28 eV. There is not an observable change in the lifetime of the state when the excitation energy is changed.

dynamics do not exhibit any signatures of accelerated relaxation dynamics (i.e., faster decay or a relative change in long-lived emission) in either the two excitation regimes within the time resolution of our setup (55 ps). We conclude that neither trapping processes nor Auger and other density-dependent recombination channels are substantially different between the two regimes.

Supplementary Note 10: Repeatability of the Enhancement Effect.

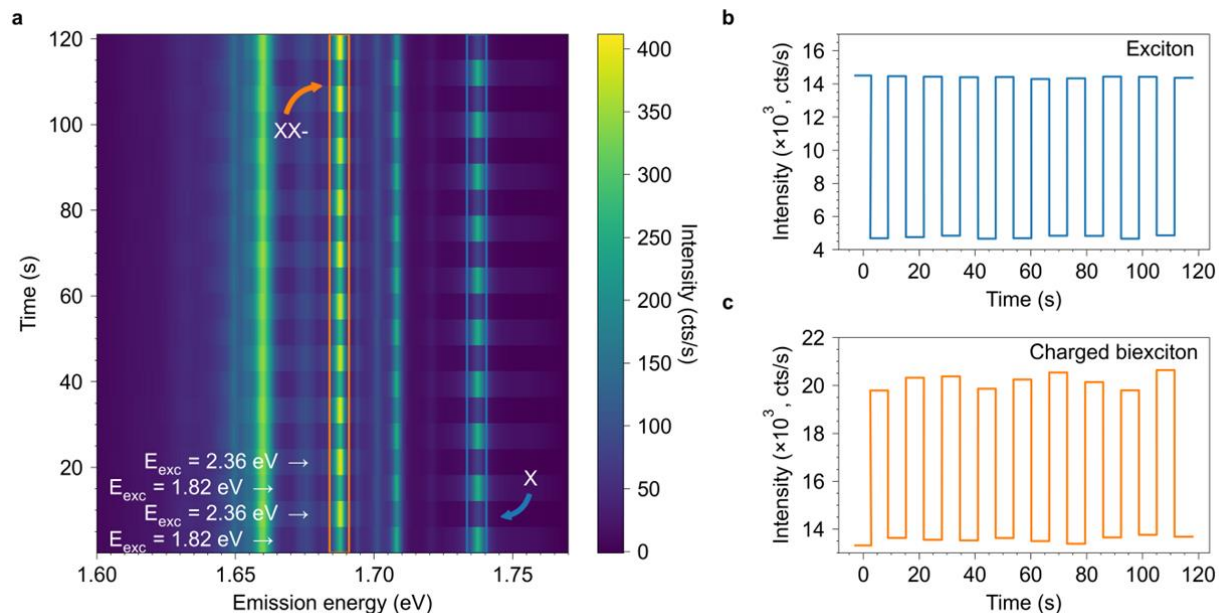


Figure S5 – Repeatability of the enhancement effect. a photoluminescence acquired while repeatedly cycling the excitation energy between 1.82 and 2.36 eV. 20 total spectra were acquired over 120 seconds. b & c, the integrated intensity of the exciton and charged biexciton, respectively, taken along the time axis of the colormap in a.

Figure S5 exemplifies the repeatability of the enhancement effect. In this measurement, the excitation energy is cycled repeatedly between 1.82 and 2.36 eV while maintaining a constant spot size and excitation density ($\rho_{\text{exc}} \approx 10^{11} \text{ cm}^{-2}$). PL spectra at the two different excitation energies were acquired in near continuous succession, as shown in the colormap in Figure S5a. The excitation laser beam was directed along a unique optical path and through independent Gaussian telescopes precisely adjusted to maintain the same spot size for each excitation energy before being recoupled into a common optical path and directed into the microscope. Rapid switching between the two excitation energies was achieved by using computer-controlled flip mirrors to select the desired optical path while simultaneously tuning the excitation energy of the laser. We estimate the

downtime between each acquisition to be less than one second. The PL spectra are highly repeatable, demonstrating that there is not a persistent build-up of static charge in the 1L-WSe₂.

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CHAPTER 4

STRUCTURE-PROPERTY RELATIONSHIPS REVEALED BY SURVEYING THE
DYNAMICS OF QUANTUM EMITTERS IN MONOLAYER WSe₂ SYSTEMSContribution of Authors and Co-Authors

Manuscript in Chapter 4

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Abstract

Two-dimensional single-layer WSe₂ is a promising material system for solid-state quantum light sources that can be deterministically positioned and integrated with a wide variety of other material systems and photonic devices. The emergence of quantum emitters in WSe₂ at cryogenic temperatures necessitates localized strain and is remarkably robust to differences in substrates, material quality, and stressors that generate the strain. However, the effects of these factors on the performance and properties of the resulting quantum emitters is unknown and is a critical knowledge gap. Comparison of individual emitters of different samples is of limited utility due to the substantial heterogeneity of emitter within a single sample. Here, using statistical comparison of emitter populations, we show that the specific architecture significantly and systematically affects the excited state dynamics of the quantum emitters formed in single-layer WSe₂. We probe the effects of material quality, substrate composition, and choice of nanoscale stressor. Although the emitters appear the same in terms of emission spectra and brightness, systematic differences in their dynamics are revealed by formulating a method to compare excited state lifetimes and photoluminescence transients of the different populations. Initial assessment of the differences suggests that the choice of substrate does not significantly alter emitter dynamics, but that non-linear relaxation dynamics are reduced in emitters hosted in high-quality WSe₂ that uses gold nanocones as stressors. The same system also significantly reduces signatures of exciton diffusion to quantum emitter sites. The study demonstrates how statistical comparison of emitter populations in WSe₂ is a key approach for understanding emitter performance, which will be necessary for engineering quantum light sources based on 2D materials.

Introduction

The generation of single photons and entangled photon pairs are integral to quantum photonic sensing, computing and communication technologies^{1, 2}. An ideal solid-state quantum light source triggers on-demand, can be miniaturized on micron/sub-micron scales, and directly interfaces with integrated photonic circuitry³. Such solid-state quantum emitters (QEs) emerge in single-layer WSe₂ (1L-WSe₂) at cryogenic temperatures (~ 4 K)⁴⁻⁸ up to 150 K⁹, and have many appealing properties as potential quantum light sources. The van der Waals nature of 1L-WSe₂ permits versatility for heterogeneous integration into on-chip photonic platforms, relaxing severe constraints imposed on other systems such as matching lattice constants. Additionally, the QE states in 1L-WSe₂ are hypothesized to retain the band-edge characteristics of excitons¹⁰⁻¹², which could eventually lead to the coupling of quantum light to exotic many-body phenomena such as excitons and their associated dynamics^{10, 11, 13-15}. Finally, the QEs in 1L-WSe₂ correlate to localized nanoscale regions of strain that include engineered nanoscale stressors¹⁶⁻¹⁹, and/or nanobubbles²⁰ and nanowrinkles²¹ which form during sample preparation. Precision nanofabrication of stressors can therefore be used to tune QE properties with strain and position them on length scales of less than 100 nm, enabling the ability to fabricate extensive microarrays²²⁻²⁴ of quantum light sources at exact locations and with small footprints.

As long as localized strain is present, the emergence of QEs in 1L-WSe₂ is ubiquitous and seemingly independent of the quality of the 1L-WSe₂ (i.e. defect density), the substrate material (e.g. hBN, SiO₂, etc.), or the method of generating the localized strain (e.g. nanobubbles, pillars, cones, nano-indents, etc.). As a result, QEs in 1L-WSe₂ have been reported in many different systems ranging from nanobubbles on an SiO₂ surface to 1L-WSe₂ draped over precisely fabricated

pillars or plasmonic systems^{23, 24}. Despite this impressive robustness, a systematic comparison of the QEs in these different systems does not exist. It is unknown how the QEs in these systems compare to one another and the extent to which they are equivalent. This critical knowledge gap is further exacerbated by the inhomogeneity and variations of individual QEs in one a single system: a single emission spectrum and anti-bunching curve is insufficient to characterize the QEs in a sample. From developing a mechanistic understanding of how the QEs form to formulating their underlying structure-property relations to optimizing their performance for quantum photonic technologies, it is imperative to compare QE populations in different systems using a robust methodology that captures systematic differences between the populations.

Here, we survey the structural and spectroscopic properties of QE populations in four different systems that are based off of 1L-WSe₂, consisting of unique permutations of material quality, supporting substrate, and stressor to generate localized strain. Neither structural characterization with atomic force microscopy (AFM) nor room-temperature photoluminescence (PL) spectroscopy reveal distinct differences between the samples. However, time-resolved PL of the QE states that emerge at cryogenic temperatures uncover a very diverse range of dynamics within each sample. Simple metrics to characterize the excited state lifetime of the QE and the analytical shape of its PL transient are developed and enable us to reconstruct the ensemble behavior of QEs in each sample from the measurements of many single QE states. Comparison of the distributions of these descriptors reveal systematic differences in the excited state dynamics of the population of QEs, depending on the exact architecture of the 1L-WSe₂-based QE system. Our preliminary interpretation of these distributions is that disorder due to non-linear kinetic processes is reduced in the samples consisting of high-quality flux-grown 1L-WSe₂ with a low defect density

and that the emitter dynamics are accelerated by using engineered Au nanocones as the choice of nanoscale stressor over naturally occurring nanobubbles and nanowrinkles. The presented methodology enables the first direct comparison of different QE systems that can be used for future efforts to optimize performance as well as gain critical insight into the nanoscale processes and structure-property relationships that dictate QE behavior in 1L-WSe₂.

Results

The four 1L-WSe₂-based quantum emitter (QE) systems studied in this work are summarized in Figure 1, which presents bright-field optical images and AFM micrographs of each sample. All 1L-WSe₂ samples were mechanically exfoliated from bulk crystals. In the first sample (Sample 1; Figure 1a), 1L-WSe₂ from a commercially-supplied bulk crystal (HQ Graphene) was dry-transferred²⁵ onto a hexagonal boron nitride (hBN) crystallite that was mechanically exfoliated from a commercially-supplied bulk crystal (HQ Graphene). To probe the influence of material quality, 1L-WSe₂ from flux-grown WSe₂ bulk crystals²⁶ was dry-transferred onto an hBN substrate (Sample 2; regions labeled “S2” in Figure 1b). Prior investigations have shown that the flux-grown 1L-WSe₂ has a defect concentration that is $\sim 100\times$ smaller than that of the commercially-supplied 1L-WSe₂²⁷. Thus, comparing QEs in Sample 1 to those in Sample 2 probes how material quality affects their properties. To also probe the influence of the dielectric environment and surface disorder, we also characterize regions of the same sample where the 1L-WSe₂ drapes off the supporting hBN crystallite and onto the underlying SiO₂. These regions are the third sample (Sample 3; regions labeled “S3” in Figure 1b). In comparison to hBN, the SiO₂ surface is significantly more disordered and has a smaller dielectric constant^{28, 29}. Thus, a comparison between Samples 2 and 3 provides means to assess how these factors influence the properties of

1L-WSe₂ QE states. Finally, the fourth sample (Sample 4; Figure 1d) consists of flux-grown 1L-WSe₂ that is deposited on an array of nanofabricated gold nanocones with individual base diameters of 120 nm, heights of 60 nm, and a radii of curvatures at the apex of the cone of 17 nm. In the array, each nanocone is separated by 500 nm.

Three aspects discriminate Sample 4 (1L-WSe₂ on Au nanocones) from the others. First, AFM characterization of the sample shows that the gold nanocones induce localized strain in the 1L-WSe₂ that is characterized by tenting at each nanocone site. The tenting at each site is further interconnected by 1D wrinkles. The array of nanocones is a deliberate and systematic way of creating localized strain to induce the formation of QEs^{4, 5, 7, 30, 31}, and the precision of the nanofabrication process yields more uniform strain patterns than the nanobubbles in Samples 1-3. Second, the metallic nanostructures can alter the excited state dynamics of nearby emissive states through excited state quenching and Purcell enhancement³⁰. Finally, a thin film (<10 nm) of gold remains on the SiO₂ surface due to incomplete etching during the fabrication process, providing another potential source of quenching and/or enhancements, especially of the unstrained 1L-WSe₂ that surrounds the tents and 1D wrinkles. Compared to Sample 4, the localized strain in Samples 1-3 originates from the nanobubbles that form during the fabrication of the samples. The AFM characterization of these samples shows that their topographic profiles are qualitatively similar. Nanobubbles that are separated by regions of atomically flat 1L-WSe₂ are found in all three samples. From the AFM alone, Samples 1-3 appear qualitatively equivalent.

Figure 1(d-f) presents PL spectra of each sample taken at room temperature. A single excitonic emission peak is observed from all samples and PL imaging with diffraction-limited resolution reveals a relatively homogeneous spectral response of each sample with only slight

variations in PL emission energy (see SI). We note that room-temperature nano-optical measurements^{32, 33} have uncovered significant sub-diffraction heterogeneity of excited-state PL in similar samples. We anticipate that similar heterogeneity exists in these samples but is unresolvable/undetectable with the far-field diffraction-limited measurements shown here.

All four samples host a spatially inhomogeneous distribution of QE states at 4 K. In each sample, the low-temperature PL is dominated by emitters in the energy range from 1.54-1.72 eV, as shown in the waterfall plots in the bottom row of panels in Figure 2. Sample 1 exhibits the lowest emission energies ($E_{\text{median}} \approx 1.62$ eV) while the emission in Samples 2-4 are blue shifted approximately 40-60 meV ($E_{\text{median}} \approx 1.66$ eV, 1.68 eV, and 1.68 eV, respectively). The emitters have narrow linewidths that span 1-8 meV. Samples 1 and 4 host the QEs with the narrowest emission lines ($\Delta E_{\text{median}} \approx 1.5$ meV and 1.25 meV, respectively) while Samples 2 and 3 exhibit quantum emission with larger linewidths ($\Delta E_{\text{median}} \approx 3.5$ meV). The distributions of emission linewidths and energies are reported in the SI. We note that 1L-WSe₂ samples that are fully encapsulated with hBN exhibit intense excitonic emission from bright and dark^{34, 35} excitons, trions, and multiexciton states in contrast to the behavior of Samples 1-4 here (that either are only half encapsulated or not encapsulated at all)³⁶⁻⁴⁰. While photonic cavity effects⁴¹⁻⁴³ make a quantitative comparison of the emitter intensities in the different samples challenging, a dramatic difference in the brightness between the four samples is not observed.

Whereas the low-temperature time-integrated PL imaging and spectroscopy measurements only resolve slight differences between the emitter linewidths and energies in the four samples, time-resolved PL spectroscopy of individual emitters reveals a much more diverse suite of behavior that is challenging to systematically contrast between the samples. This heterogeneity is

demonstrated in Figure 3 which shows three representative PL transients observed from different QEs in Sample 1. For these measurements, individual emitters were spectrally isolated by a monochromator and then directed to a time-correlated single-photon counting apparatus (see methods for details). The PL spectra of the emitters whose dynamics were measured are shown in the waterfall plots in Figure 2. We observe dynamics with biexponential (Fig. 3a), monoexponential (Fig. 3b), and delayed onset (Fig. 3c) characteristics. Similar heterogeneous dynamics are present in the other samples.

The varied emitter dynamics poses a major challenge to comparing the temporal behavior of the emitters in the different samples: any comparison must be done using a statistical approach that can uncover systematic variations on emitter dynamics from one sample to the next. Ideally, a quantitative rate model with coupled sub-populations of excitons that includes linear and nonlinear terms in both the excitation and relaxation processes of the QEs is able to capture the heterogeneity in the dynamics of individual emitters⁴⁴⁻⁴⁶ (see SI for examples of rate modeling). However, ascribing meaningful physical significance and origins of the obtained rates is ambiguous, making a comparison of the statistical distributions of their rates in the different samples fraught with potential pitfalls. For instance, one challenge is that the formation mechanism of the QE states is still not unambiguously established^{10, 47}. Second, the observed dynamics likely convolve many significant factors including diffusion and strain-induced funneling of excitons to the QE sites⁴⁸⁻⁵⁰, strain-enhanced emission dynamics of localized excitons⁴⁷, Purcell enhancement/modification of the local density of photonics states⁵¹⁻⁵³, and excited state quenching due to interaction with the surrounding environment and non-radiative defects⁵⁴. Because of these ambiguities, further experimental and theoretical investigations must be performed to understand

the roles of such phenomena in the formation, excitation, and excited-state relaxation of QEs before a quantitative model that can be applied to different systems can be established. In the absence of such a model, we turn to two empirical descriptors of the dynamics that capture the variations in lifetimes and analytical form of the PL transients, allowing us to statistically compare the dynamics of the QE populations in each sample.

As summarized in Figure 4, the quantity which we term the effective lifetime, t_{eff} , describes the statistical variation of the overall rate of relaxation of the individual QEs between the four samples. The effective lifetime is determined by the time it takes for the QE PL to decay to 36% of its intensity immediately after photoexcitation (i.e., a fractional decrease in intensity of e^{-1} from time $t = 0$ ns). Two example transients from Sample 1 are shown in Figures 4a and 4b with effective lifetimes of 1.0 ns and 3.6 ns, respectively. The statistical distributions of the effective lifetimes of individual QEs for all four samples are shown in Figure 4c. Sample 1 (commercial 1L-WSe₂ on hBN) exhibits the largest spread of effective lifetimes. The spread in effective lifetimes is reduced in Sample 2 (flux-grown 1L-WSe₂ on hBN), suggesting that the reduction of defect density leads to a more uniform distribution of relaxation rates. The distribution of effective lifetimes in Sample 3 (flux-grown 1L-WSe₂ on SiO₂) matches that of Sample 2 (also flux-grown 1L-WSe₂ but on hBN), suggesting that interfacial disorder associated with a SiO₂ surface does not significantly alter the relaxation rates of the emitters. In Sample 4, the effective lifetimes are systematically shorter than in Samples 1-3. The statistical distribution of effective lifetimes reflects acceleration of the excited state relaxation that is anticipated for emitters near metallic films and nanostructures due to quenching and Purcell enhancement. We note that the overall brightness of the QEs in Sample 4 is comparable to the other samples, indicating that the

faster relaxation rate in this sample could result in QE systems with larger emission rates under steady-state excitation.

In addition to the effective lifetime, Figure 5 shows that there is a systematic difference between the analytical forms of the PL transients of QEs in the different samples. To characterize the shape, integer multiples of the effective lifetime are used to divide the PL transients into different epochs relative to $t = 0$ ns. The ratio, R , between the integrated intensity of the second epoch ($t_{eff} \leq t \leq 2t_{eff}$) to that of the first epoch ($0 \leq t \leq 2t_{eff}$) characterizes the relative shape of the PL transient:

$$R = \frac{\int_{t_{eff}}^{2t_{eff}} I(t) dt}{\int_0^{t_{eff}} I(t) dt}$$

For a perfect monoexponential decay, the ratio evaluates to $R = 0.37$. Figure 5a shows a PL transient from an example QE in Sample 1. This emitter exhibits a pronounced delay after $t = 0$ ns before reaching its maximum emission rate at $t \approx 500$ ps. We attribute this delayed onset to strain-induced funneling of excitons to the emitter site, which introduces a delay between the development of the maximum emission rate and the initial photoexcitation of the surrounding area. The ratio for the PL transient in Figure 5a evaluates to $R = 0.26$, which is smaller than the perfect exponential. In stark contrast, Figure 5b shows an example PL transient from a QE in Sample 1 that exhibits quasi-instantaneous rise in the PL intensity at $t = 0$ followed by rapid decay that cannot be described by a simple monoexponential function. For this QE, the decay is biexponential-like which we attribute to a nonlinear contribution in the decay kinetics. Because we spectrally isolate the narrow emission bands for individual emitters, the probability that two independent emitters with distinct lifetimes (which would also lead to biexponential decay) is

negligible. For this biexponential-like decay transient, the ratio evaluates to $R = 0.70$ which is larger than the perfect exponential. Further analysis of the entire population of emitters that is presented in the SI confirms that the ratio, R , reliably characterizes the shape of the PL transient as exemplified here with the emitters in Figures 5a and 5b, providing means to statistically compare these transients across the different samples.

Figure 5c reports the statistical distributions of ratio R that characterizes the shape of the PL transient for each of the four samples studied in this work. The emitters in Sample 4 (1L-WSe₂ on Au nanocones) are tightly-grouped around $R = 0.4$, indicating that most emitters in this sample exhibit monoexponential decay dynamics without a delayed-onset. In contrast, the emitters that are hosted in Sample 1 (commercial 1L-WSe₂ on hBN) exhibit the full suite of transients with delayed onsets, mono-exponentials decays, and biexponential-like decays. The emitters that are hosted in the flux-grown 1L-WSe₂ in Samples 2 and 3 have PL transients with delayed onsets, suggesting that significantly more exciton diffusion to emitter sites occurs in this emitter-host permutation. This trend could be qualitatively explained by a reduced density of QEs in Samples 2 and 3 which would amplify the role of exciton diffusion in pumping the emitters, but the spatial density of emitters is approximately the same in all sample regions measured. Alternatively, the lower defect density in the flux-grown 1L-WSe₂ may promote longer excited state lifetimes (which is consistent with the results in Figure 4), enabling the free excitons to diffuse over greater distances and enhancing the ability for an emitter to collect excitations from the surrounding material. In terms of disorder, Sample 4 (1L-WSe₂ on Au nanocones) exhibits the tightest distribution for both the shape ratio (R) and the effective lifetime (t_{eff}), indicating that even though there is significant structural heterogeneity from the tenting and networks of wrinkles, the

systematic generation of strain with the nanocone arrays results in a more uniform distribution of emitters in terms of their dynamics, potentially without sacrificing emitter brightness.

Conclusion

In conclusion, we have used two numerical metrics to classify the dynamics of QEs hosted in 1L-WSe₂. The first metric, the effective lifetime, classifies the characteristic speed of the excited state dynamics, whereas the second metric, which describes the distribution of intensity in time relative to the effective lifetime, classifies the shape of the photoluminescence transient. We use these metrics to statistically compare the populations of QEs in four samples of 1L-WSe₂ with different material qualities, substrates, and nanoscale stressors. The statistical comparison reveals differences in the populations that are undetectable without such a statistical approach, demonstrating that the architecture of the 1L-WSe₂ system has important and non-negligible effects on the QEs that it hosts. Our initial analysis of the differences suggests several key structure-property relationships. First, relaxation dynamics that are characteristic of nonlinear processes (such as Auger recombination) appear to be reduced in emitters hosted in high-quality WSe₂. Second, straining high quality 1L-WSe₂ with an array of Au nanocones reduces the signature of delayed emission that is likely due to excitons diffusing to an emissive site. And third, the dynamics are overall accelerated in the sample consisting of high quality WSe₂ strained by Au nanocones signifying the combined effects of Purcell enhancement and metal-induced quenching. This work demonstrates how optimization and investigations of QEs in 2D materials are strengthened by identifying systematic differences in the populations. The identified unambiguous difference in the populations of QEs prove that statistically significant engineering of QEs in 1L-

WSe₂ is achievable through the design of the QE architecture, laying important groundwork for future studies of QEs in 2D materials.

Supporting information: Materials and methods; details of sample fabrication^{27, 55} and optical measurements, additional optical data and discussion to support the assignment of QE states, statistics of the QE energies^{56, 57} and linewidths⁵⁸⁻⁶⁰, validation of accurate classification of the shapes of PL transients by the intensity ratio metric, rate model analysis of excited state dynamics, and corner plots of the dataset of QE properties.

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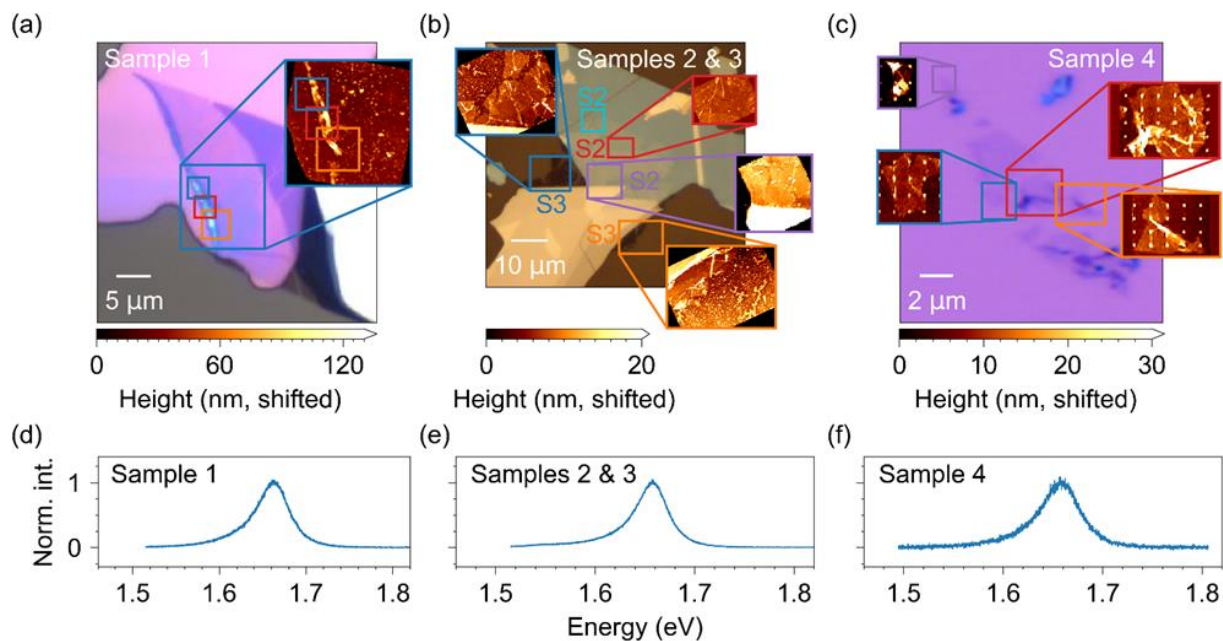


Figure 1 – Summary of QE samples. (a-c) Bright field optical micrographs of the samples 1-4 with AFM height maps of selected regions inset. (a) Commercially grown 1L-WSe₂ supported by hBN. (b) Flux-grown 1L-WSe₂ supported by hBN (regions labeled “S2”; Sample 2) and SiO₂ (regions labeled “S3”; Sample 3). (c) Flux-grown WSe₂ on an array of Au nanostressors. (d-f) Representative photoluminescent spectra taken at room temperature for each sample.

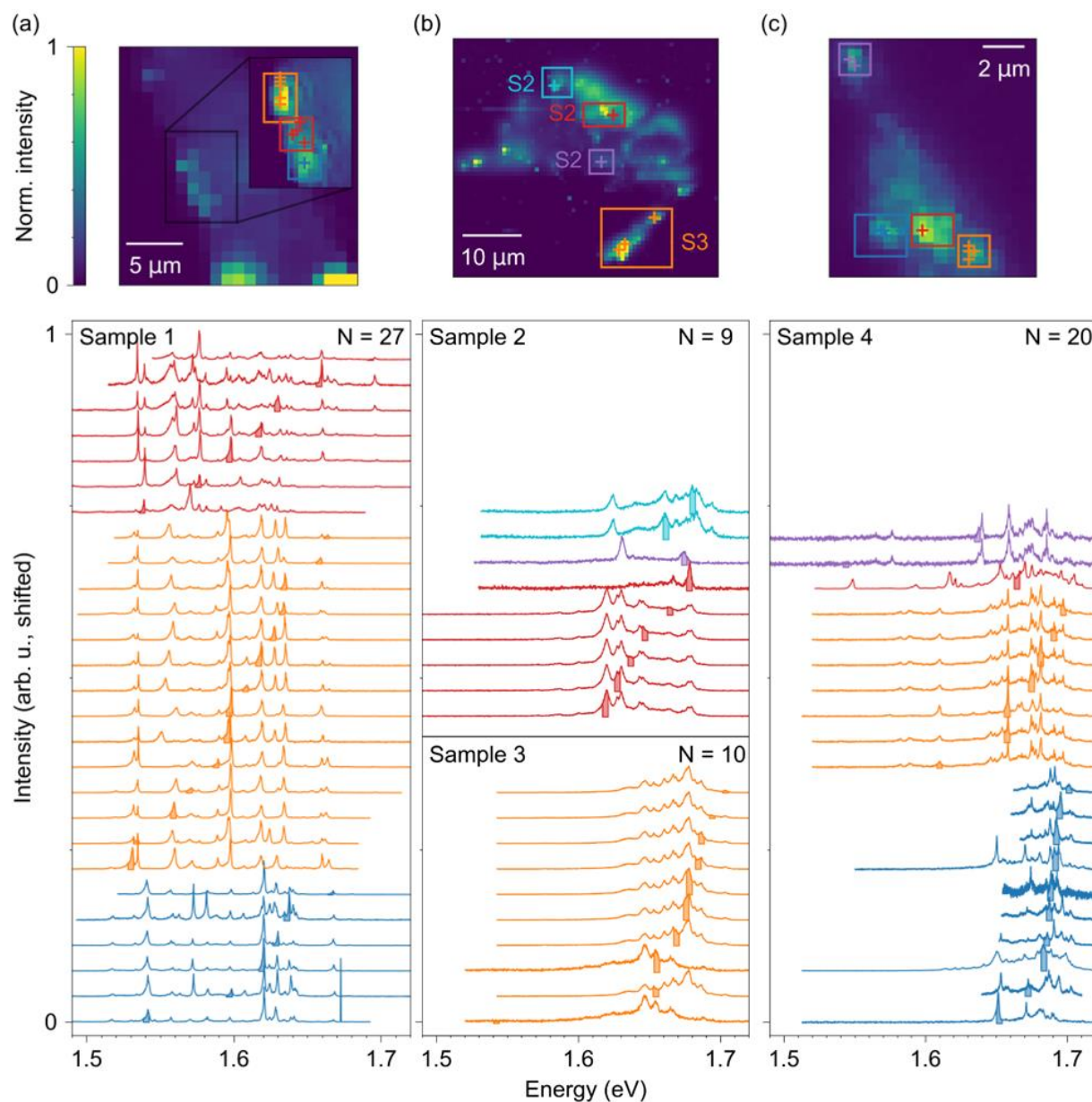


Figure 2 – Low-temperature photoluminescence (PL). (a-c) Top row, spatial maps of integrated PL intensity measured from each sample at $T = 4$ K. Each color-coded region is at the same approximate location as in Figure 1. (a-c) Bottom row, PL spectra taken from the points denoted by the color-coded cross annotations in the maps. Each spectrum was acquired successively with the measurement of the PL time-transient of the emitter denoted by the shading under the PL spectrum. $N = 27$ PL transients were measured from Sample 1, $N = 9$ from Sample 2, $N = 10$ from Sample 3, and $N = 20$ from Sample 4.

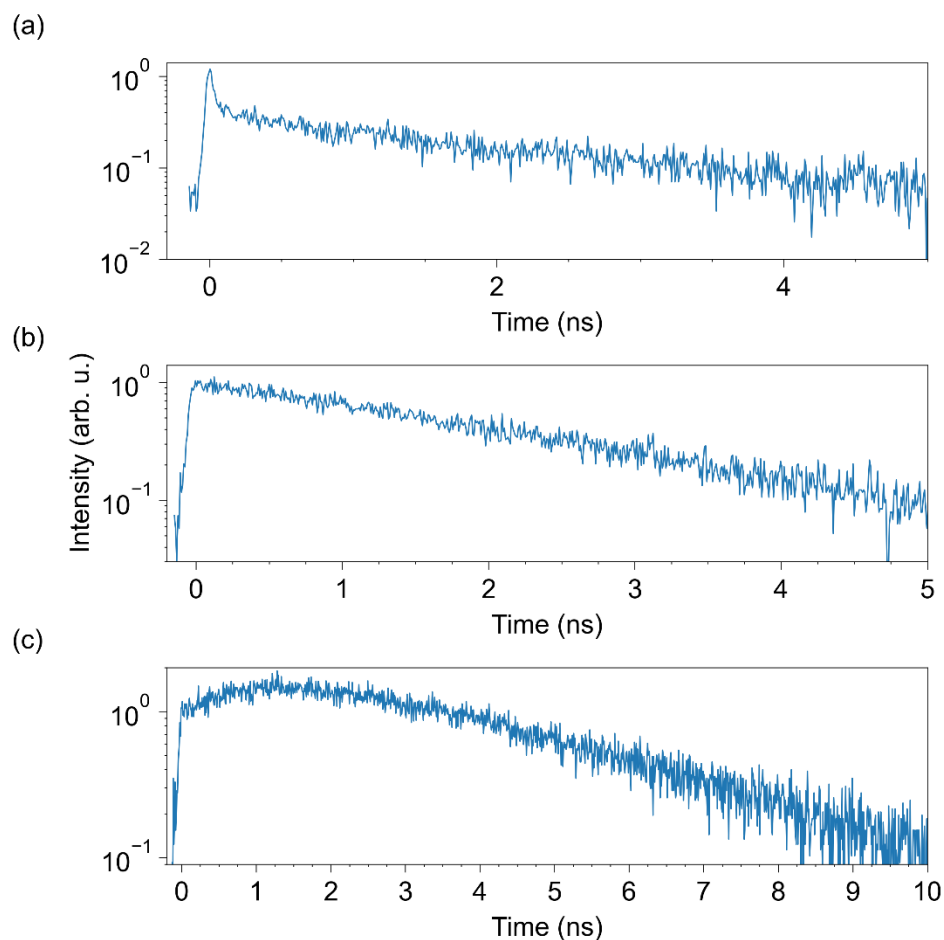


Figure 3 – Example photoluminescent transients that demonstrate the variety of kinetics measured. (a) A representative PL transient that exhibits strong biexponential decay characteristics. (b) A representative monoexponential PL transient. (c) A representative transient that exhibits a delayed onset of emission.

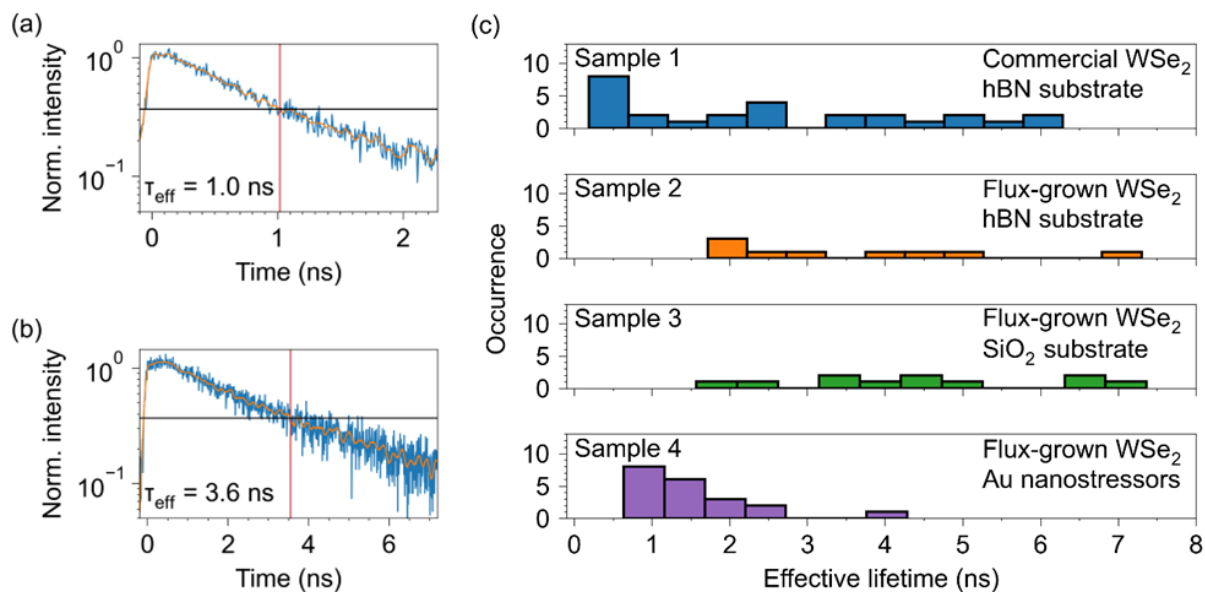


Figure 4 – The statistical distribution of effective lifetimes of the emitters measured for each sample. (a) An example photoluminescent transient that exhibits a relatively fast effective lifetime ($\tau_{\text{eff}} = 1$ ns) and (b) an example PL transient that exhibits a longer effective lifetime ($\tau_{\text{eff}} = 3.6$ ns). The horizontal line indicates the threshold intensity level that defines the effective lifetime ($I/I_0 = e^{-1} \approx 0.36$). The vertical red line shows the value of τ_{eff} for each emitter. The raw experimental data is plotted in blue and the data smoothed by a Savitzsky-Golay filter is shown in orange. (c) Histograms of the effective lifetimes of the emitters measured from each sample.

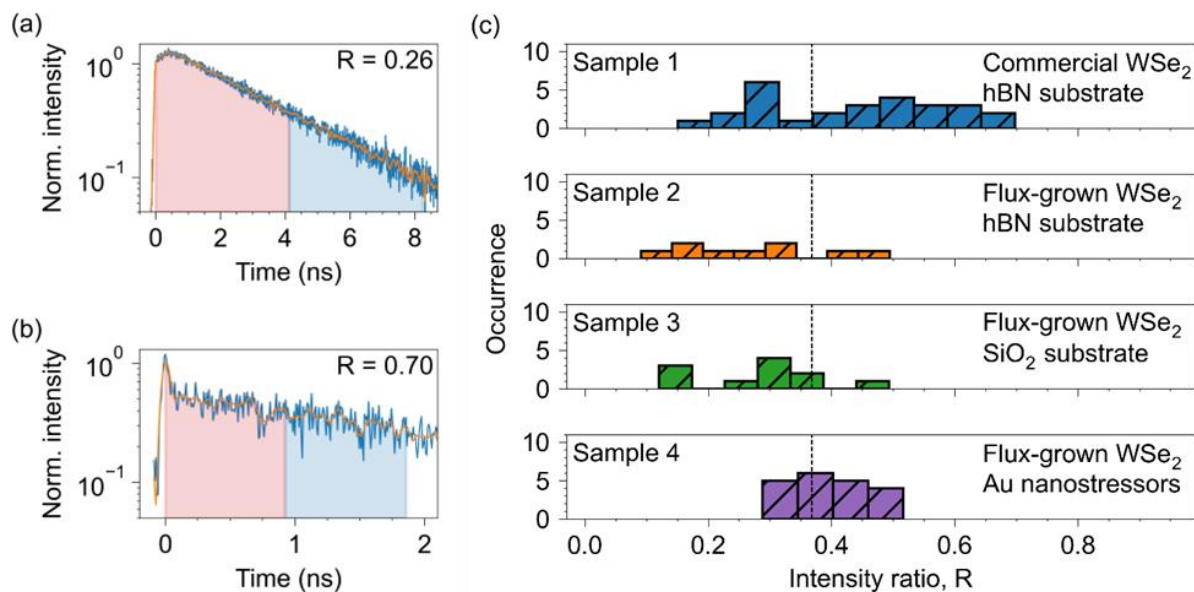


Figure 5 – The statistical distribution of intensity ratio, R , which is the ratio of intensity in the second interval of the decay trace to that of the first. (a) An example photoluminescent transient that exhibits a delayed onset characteristic. This is captured by $R = 0.26$. (b) An example PL transient that exhibits biexponential-like decay. This is captured by $R = 0.70$. The shaded regions denote the bounds of integration for each epoch in the calculation of R . (c) Histograms of R for the emitters measured from each sample.

Supporting Information for: A Statistical Survey of Excited State Dynamics of Quantum Emitters
in Monolayer WSe₂

Contents

- S1. Materials and methods**
- S2. Additional evidence of quantum emission**
- S3. Additional room temperature photoluminescence characterization**
- S4. Statistics of the QE energies**
- S5. Statistics of the QE linewidths and deviations from the transform limit**
- S6. Validation of the classification of the kinetics by the intensity ratio metric**
- S7. Additional discussion of the metrics used to classify excited state dynamics**
- S8. Rate model analysis of excited state dynamics**
- S9. Additional cross sections of the QE dataset**

S1. Materials and Methods

Sample Fabrication Sample 1 was fabricated through the dry transfer of WSe₂ flakes using a viscoelastic polydimethylsiloxane (PDMS) stamp. The hBN and WSe₂ flakes (HQ Graphene) were mechanically exfoliated onto separate substrates: hBN onto a silicon substrate with 100 nm of oxide and WSe₂ onto a PDMS stamp, respectively. Subsequently, the 1L-WSe₂ was identified under an optical microscope and transferred onto a thick hBN flake.

Sample 2 (3) was also prepared using mechanically exfoliated flakes of WSe₂ and hBN; however, the bulk WSe₂ crystals were flux-grown and have much lower defect densities compared to the commercial CVT-grown crystals¹. The layers were picked up using PCL² on top of a PDMS stamp and transferred onto a silicon substrate with 90 nm of oxide. The sample was then placed in a hot (90° C) acetone bath for 1 hour to remove the remaining polymer, followed by a rinse in IPA and dried with compressed nitrogen.

The same transfer methodology was used for Sample 4, but without hBN underneath the 1L-WSe₂. In brief, a layer of gold was evaporated onto a silicon wafer, and electron-beam lithography was used to open circular holes in a layer of PMMA on top. This was followed by

deposition of aluminum oxide and lift-off, leaving a hard mask of Al_2O_3 disks behind. Argon ion milling was then used to produce the gold nanocone structures.

Optical Measurements *Room temperature photoluminescence spectroscopy.* Light from a 532 nm CW diode laser (Cobalt Samba) was focused onto the samples using an Nikon 40x objective (NA = 0.6), spot size $\approx 1 \mu\text{m}$ FWHM. Luminescence was collected in a back-scattered geometry and directed to a Czerny-Turner optical spectrometer, dispersed with a mechanically ruled grating (groove density = 600 g/mm), and measured with a scientific CCD camera (Andor iDus 416, cooled to -55 °C) after laser light was rejected by using a series of interference filters. PL mapping was conducted by scanning the beam over the sample using a 4f-imaging system in conjunction with a 2-axis galvonometric scan mirror.

Cryogenic Photoluminescence Spectroscopy. Cryogenic measurements ($T = 4 \text{ K}$) were conducted by cooling the samples in a closed-cycle liquid helium cryostat with optical access (Montana Instrument S50 cryostation). The samples were illuminated with pulsed laser light generated from a supercontinuum fiber laser (NKT photonics SuperK EXTREME, pulse width = 55 ps, rep. rate = 78 MHz) that was filtered with an acoustic-optic tunable filter (Gooch and Housego) to 540 nm (filter bandwidth $\approx 4 \text{ nm}$). The fluorescence was filtered and measured as described for the room-temperature photoluminescence measurements.

Time-resolved measurements. The sample was illuminated with pulsed laser light generated from a supercontinuum fiber laser (NKT photonics SuperK EXTREME, pulse width = 55 ps, rep. rate = 78 MHz) that was filtered with an acoustic-optic tunable filter (Gooch and Housego) to 540 nm (filter bandwidth $\approx 4 \text{ nm}$). Light was collected as described above and filtered using a monochromator exit port on a Czerny-Turner optical spectrometer (Horiba iHR320,

monochromator bandwidth ≈ 4 meV). The light was then optically relayed onto a single-photon avalanche photodiode (MPD photonics, timing jitter ≈ 25 ps). Time-correlated single-photon counting was achieved by using ultra-fast time-tagging electronics (PicoQuant HydraHarp 400) which generated histograms the detection events from the avalanche photodiode with respect to a synchronizing pulse from the laser.

S2. Additional Evidence of Quantum Emission

Here we present corroborating evidence that the emitters measured in this work are likely single-photon emitters (also known as single quantum emitters, which we abbreviate as QEs here and in the main text). This section is divided into three parts: 1 – Differentiation from unlocalized excitons using excited state lifetimes, 2 – Resolution-limited spatial localization of the narrow emission lines, and 3 – Evidence for ubiquitous emitter blinking and spectral diffusion.

1 – Differentiation from Unlocalized Excitons Using Excited State Lifetimes The QEs measured here have significantly longer lifetimes than what is typically reported for the free excitons in WSe₂. Excited state lifetimes of free exciton complexes excitons in high-quality materials typically range from 10 ps – 300 ps³. Stronger non-radiative decay channels in low quality materials further accelerate these dynamics, which validates that the extended lifetimes measured across the 4 samples in this work cannot be consistent with the dynamics of free exciton complexes.

2 – Spatial Localization of the Narrow Emission Lines The emitters are approximately localized to resolution-limited spatial regions on the samples. This is demonstrated in Figs. S1-

S3 where we present hyperspectral maps of the QE photoluminescence. The integrated PL intensity is shown in panel (a) in each figure.

To remove broad background luminescence from the hyperspectral maps, we decompose the hyperspectral maps using singular value decomposition and identify the strongest eigen component that contributes to the broad background emission. This component is shown in panels (b). We then reconstruct the hyperspectral map with that component removed.

Finally, we spectrally filter the reconstructed hyperspectral maps by sweeping a 2 nm band across the spectra. Panels (c) present a mosaic of filtered hyperspectral maps for selected band centers. In these filtered maps, we observe spatial-spectral inhomogeneity on the order of the spatial resolution on the optical setup ($\approx 1 \mu\text{m}$).

3 – Evidence for Ubiquitous Emitter Blinking and Spectral Diffusion Figure S4 presents four representative steady-state PL time series. These measurements consist of a series of PL spectra being acquired in near-continuous succession. For most of the emission features measured in these datasets, blinking and/or spectral diffusion is observed.

Both blinking and spectral diffusion are strong indicators that these emission features should be attributed to QEs as opposed to unlocalized excitons. When measuring the PL from unlocalized excitons, emitter inhomogeneity due to perturbations of the local environment of any single exciton is averaged over the ensemble of emitters within the collection area of the measurement. In contrast, there is no ensemble averaging when measuring a QE, and the emission from can be significantly shifted in energy (i.e., spectrally diffuse) or (de)activated (i.e., blink) on the timescale of seconds due to persistent photodoping, the adsorption of molecules onto the 2D material, and other slow thermal, mechanical, or chemical processes. We note that the precise

mechanism that causes the emitters to blink and spectrally diffuse is not well established. Nevertheless, the observation of blinking and spectral diffusion is consistent with the assignment of QEs.

S3. Additional Room Temperature Photoluminescence Characterization

Figure S5 presents spatial maps of the photoluminescence intensity of each sample taken at room temperature. The regions of interest where quantum emission was measured at low-T are denoted by the box annotations overlaid on the PL intensity maps. The waterfall plots in the bottom row of the Figure S5 show representative PL spectra from the regions indicated on the spatial maps.

Most regions show a nominally homogeneous spectral response, with only slight variations in emission energy across both the spatial extent of a single sample and between the samples. There is, however, a region in Sample 3 where we observed significantly red-shifted PL emission. This region is denoted by the blue ROI in Figure S5(b), and the corresponding PL spectrum is plotted in blue in the corresponding waterfall plot. We speculate that this region consists of bilayer Wse₂. At low temperatures we observe low-energy ($E < 1.55$ eV) narrow emission from this region, also. We hypothesize that this region hosts deep level trap states that result in low energy quantum emission and have removed it from the data set in the main manuscript since the emitter is likely hosted by a two-layer system.

S4. Statistics of the QE Energies

The distribution of the energies of the emitters characterized with TCSPC are presented in Figure S6. Sample 1 has the most diverse distribution of emitter energies while Sample 2-4 have similar spreads

in energy. Notably, the energy of the emitters tends to increase in each sample (i.e., Sample 1 has the lowest median emitter energy and Sample 4 has the highest median emitter energy).

The large spread of emitter energies in Sample 1 is consistent with there being a diversity of localization mechanisms in the lower-quality material. For example, we hypothesize that the lowest energy emission in Sample 1 is from atomic-like transitions between in-gap donor-acceptor pairs whereas the highest energy emission is from excitons localized by shallow defects or weak strain gradients.

In contrast, Samples 2-4 do not have the low energy emission observed in Sample 1. We tentatively attribute this to the significantly decreased concentration of crystalline defects in these samples. However, in Samples 2-4 we expect the emission to arise from mostly strain-localized excitons. The energy of strain-localized excitons is predominately set by the magnitude of the material strain, which lowers the energy of the bandgap by 100 meV per 1% biaxial strain⁴⁻⁶.

In addition to the localization mechanism modifying the energies of the QE, there is also the possibility that the choice of substrate modifies the QE energy due to changes in the local dielectric environment⁷. However, we do not think that this plays a significant role in modifying the distribution of QE energies. This is evidenced by the similarity of the emitter energies in Sample 2 (High-quality WSe₂ on hBN) and Sample 3 (High-quality WSe₂ on SiO₂), which the primary difference between the two samples is the supporting substrate. Furthermore, the exciton Bohr radius (1 nm – 2 nm) is the characteristic length scale at which dielectric screening will play a significant role in modifying the binding energies of the states. Since the QEs are hosted in wrinkles or bubbles that are elevated above the surface of the substrate that supports the 2D material, we speculate that the choice of substrate plays a less significant role in the emitter energy than the localization mechanism (i.e., localization due to defects versus strain).

S5. Statistics of the QE Linewidths and Deviations from the Transform Limit

Estimates of the linewidth of the emitters measured are shown in Figure 7(a). Samples 1 and 4 have the narrowest emitter linewidths, which are grouped around 1.5 meV, while Samples 2-3 exhibit much larger linewidths and a much broader distribution.

As a rough estimate of inhomogeneous broadening, we also calculated the product of the emitter linewidth, ΔE , and one-half of the decay lifetime, Δt , for each emitter. Scaling the product ($\Delta E \Delta t$) by the reduced Plank's constant, $\hbar$, yields a rough measure of how close the emitter linewidth is to the transform limited linewidth and is shown in Figure S7(b). In this analysis, we assume that the phase relaxation time of the emitters (i.e., T_2) is one half the characteristic decay time measured experimentally (i.e., the measured dynamics are representative of T_1). Furthermore, for emitters whose excited state dynamics exhibit nonlinear dynamics we use the characteristic decay time of the slow mono exponential tail instead of the effective lifetime measured from the onset of PL emission. We measure the closest to transform limited traces in Samples 1 and 4 while Samples 2 and 3 have $2\times - 3\times$ larger values for $\Delta E \Delta t / \hbar$. We hypothesize that this could be due to two different mechanisms: 1 – Slow pumping of inherently fast QEs and/or 2 – inhomogeneous broadening due to spectral diffusion. Inhomogeneous broadening could be significant in all samples since the emitters blink and spectrally diffuse. More precise measurement utilizing photon echo and four-wave-mixing techniques are necessary to unambiguously determine the degree to which the emitters are inhomogenously broadened.

Additionally, the slow pumping of inherently fast QEs increases $\Delta E \Delta t / \hbar$ by disconnecting the characteristic decay time measured in the TCSPC experiment from the intrinsic decay times of the QE. Rather, the characteristic rate at which the emitter is pumped is measured experimentally

(see section S8 for analytical modeling). So, the approximation that the phase relaxation time is equal to half the lifetime that is experimentally measured is only valid for emitters whose excited state dynamics are not significantly slowed by pumping from a meta-stable state. We hypothesize that in Samples 2 and 3 there is significant exciton diffusion that slows the measured excited state dynamics compared to the intrinsic recombination rates. Whereas in Sample 4, the effects of exciton diffusion are reduced due to quenching by the metallic substrate and greater strain gradients. Moreover, Sample 1 should have reduced exciton diffusion due to disorder which, combined with the elongated lifetime of defect localized excitons, could make the characteristic time measured experimentally a more accurate measure of the intrinsic excited state dynamics.

S6. Validation of the Classification of the Kinetics by the Intensity Ratio Metric

Figure S8 displays a histogram of the intensity ratio metric, R , of each time-transient measured in this work. The panels adjacent to the histogram plot the mean time-transient for each bin in the histogram. As R increases, there is a clear transition from traces with a delayed onset of intensity, to monoexponential decays, to biexponential decays. Note that the horizontal axis of these plots is scaled by the effective lifetime of the emitters.

S7. Additional Discussion of the Metrics used to Classify Excited State Dynamics

The transient dynamics of the individual QE states can be classified using two primary traits. The first is their durations or effective lifetimes which span from >10 ns to less than 1 ns as shown in Figure S9a. The second is the analytical form of the photoluminescence transient. For instance, the QE in Figure S9b exhibits biexponential-like decay which is evidenced by a fast component that dominates the kinetics immediately following pulsed excitation and subsequently

transitions to a slow component that dominates at extended delay times. In contrast, in Figure S9c, the PL of the QE decays monoexponentially after a brief buildup of the signal after photoexcitation. In these panels (Figs. S9b and S9c), the horizontal axis is scaled such that the effective lifetime of the emitter is equal to 1. This scaling enables the direct comparison of the forms of decay traces that have different effective lifetimes. Finally, a monoexponential decay function with an effective lifetime equal to that of the emitter (i.e., e^{-x} where x is unitless on the scaled horizontal axis) is overlaid on each plot. The residual between the monoexponential decay and the experimental data demonstrates a simple, yet important, qualitative takeaway: decay traces with biexponential-like characteristics tend to shift intensity towards longer delay times whereas decay traces with a slow build-up of emission tend to shift intensity towards shorter delay times. This phenomenon is illustrated by the shading in Figs. S9b and S9c which indicates a deficit (red) or surplus (blue) of intensity relative to the equivalent monoexponential decay function and by the arrow annotations which denote the overall flow of intensity along the decay trace.

S8. Rate Model Analysis of Excited State Dynamics

Here we analyze minimal phenomenological rate models to qualitatively reproduce the excited state dynamics that we observe experimentally.

1 – Linear Kinetics Here, the model consists of a single exciton population which decays linearly (i.e., the decay terms scale linearly in the population) that is directly pumped. With sufficiently short pumping times (i.e., $\delta I \approx 0$) the solution to this model is a single exponential decay with a characteristic time constant of $\tau = 1/k_1$. This model reproduces TRPL dynamics of efficiently pumped states which decay efficiently through linear channels (e.g., luminescence and Shockley-Reed-Hall recombination).

$$\frac{dn_1}{dt} = I - k_1 n_1$$

2 – Nonlinear Kinetics The addition of a nonlinear decay term to the recombination channels in the rate model qualitatively reproduces quasi biexponential-like dynamics. Here, we assume a decay term that is quadratic in the population density:

$$\frac{dn_1}{dt} = -Ak_2 n_1^2 - k_1 n_1$$

Numerical solutions to this nonlinear system for a range of non-linear to linear decay rates are graphed in Figure S9(a). These simulations show that the fast component in the dynamics is tunable by choosing the relative strength of k_2 to k_1 .

At very high densities, the quadratic term dominates the kinetics, and the solution is well approximated as a power-law decay:

$$n_1 = \frac{1}{A(1 + k_2 t)}$$

At low densities, the quadratic term rapidly goes to zero and the solution approaches a single exponential decay, as discussed above. So, the solution has two characteristic time scales that are defined by k_2 and k_1 . It is common to approximate the power-law solution as:

$$n_1 = \frac{1}{A(1 + k_2 t)} \approx \frac{1 - k_2 t}{A} \approx A^{-1} e^{-k_2 t}$$

So that a biexponential model well approximates the nonlinear dynamics at short timescales and the linear dynamics at long timescales:

$$n_1 = c_0 e^{-k_2 t} + c_1 e^{-k_1 t}$$

3 – Coupled Sub-Populations Here we analyze a system which consists of coupled sub-populations of excitons. In this model, the sub-population n_1 can decay linearly at a rate of k_1 and linearly pumps the sub population n_2 at a rate of k_{1-2} . The sub population n_2 can linearly decay at a rate of k_2 . In this model, n_1 may be thought of as a long-lived population of dark excitons that are being captured by a QE state, n_2 .

$$\frac{dn_1}{dt} = -k_1 n_1 - k_{1-2} n_1$$

$$\frac{dn_2}{dt} = k_{1-2} n_1 - k_2 n_2$$

We solve this system with the eigenvalue method, which yields solutions:

$$n_1 = c_0 e^{-(k_1+k_{1-2})t}$$

$$n_2 = \frac{c_0 e^{-(k_1+k_{1-2})t}}{\frac{k_2-k_1}{k_{1-2}} - 1} + c_1 e^{-k_2 t}$$

Assuming an initial condition at $t = 0$ s of $n_1 = n_0$, $n_2 = 0$, we arrive at the solution for the IVP:

$$n_1 = n_0 e^{-(k_1+k_{1-2})t}$$

$$n_2 = \frac{n_0}{1 - \frac{k_2-k_1}{k_{1-2}}} (e^{-k_2 t} - e^{-(k_2+k_{1-2})t})$$

From the solution for n_2 , we identify that the delayed onset characteristic comes from the competing exponential terms. We define the characteristic delay time of the onset as the time that maximizes n_2 :

$$t_c = \frac{\ln\left(\frac{k_1 + k_{1-2}}{k_2}\right)}{k_1 + k_{1-2} - k_2}$$

If we assume that there is no appreciable decay of n_1 through the linear decay channel k_1 (i.e., $k_1 = 0$):

$$t_c = k_2^{-1} \frac{\ln\left(\frac{k_{1-2}}{k_2}\right)}{k_{1-2}/k_2 - 1}$$

And finally, at long delay times, the slower of the two exponential terms will dominate. So, the characteristic timescale of the exponential tail of a QE that is slowly pumped will be that of the pumping rate. Figure S9(b) plots a series of numerical solutions of these equations for different pumping rates, which demonstrates the dependence of the rise time on the relative strength of the pumping rate to the decay rate of the QE.

In summary, we've analyzed three different rate models to qualitatively reproduce the dynamics that are observed in our experiments. From this analysis we conclude that biexponential dynamics stem from nonlinear decay kinetics (e.g., auger recombination) and that the delayed onset characteristic is indicative of slow exciton diffusion into QE states.

S9. Additional Cross Sections of the QE Dataset

Figure S11 presents corner plots of the 4-dimensional dataset we have compiled in this work. Each of the panels in the interior of the figure plots one pair of parameters against one another for each sample. The panels in each row share the same vertical axis whereas the panels in each column share a horizontal axis. The stacked histograms along the diagonal of the figure plot the distribution of the parameter corresponding to the column that the histogram is in.

Qualitatively, the spread of the dataset for Sample 4 (high-quality WSe₂ on Au cones) is the most homogenous. This is evidenced by the relatively tighter groupings of the data in each corner

plot. In contrast, the distributions for Samples 1, 2, and 3 exhibit a large amount of scatter across each slice of the configuration space.

Finally, we note that the intensity ratio metric (R) and the effective lifetime (t_{eff}) are anticorrelated. I.e., emitters that have a higher value of R tend to have a shorter effective lifetime. This is expected since the intensity ratio metric captures the difference between nonlinear and diffusive kinetics which tend to occur on relatively faster and slower timescales, respectively.

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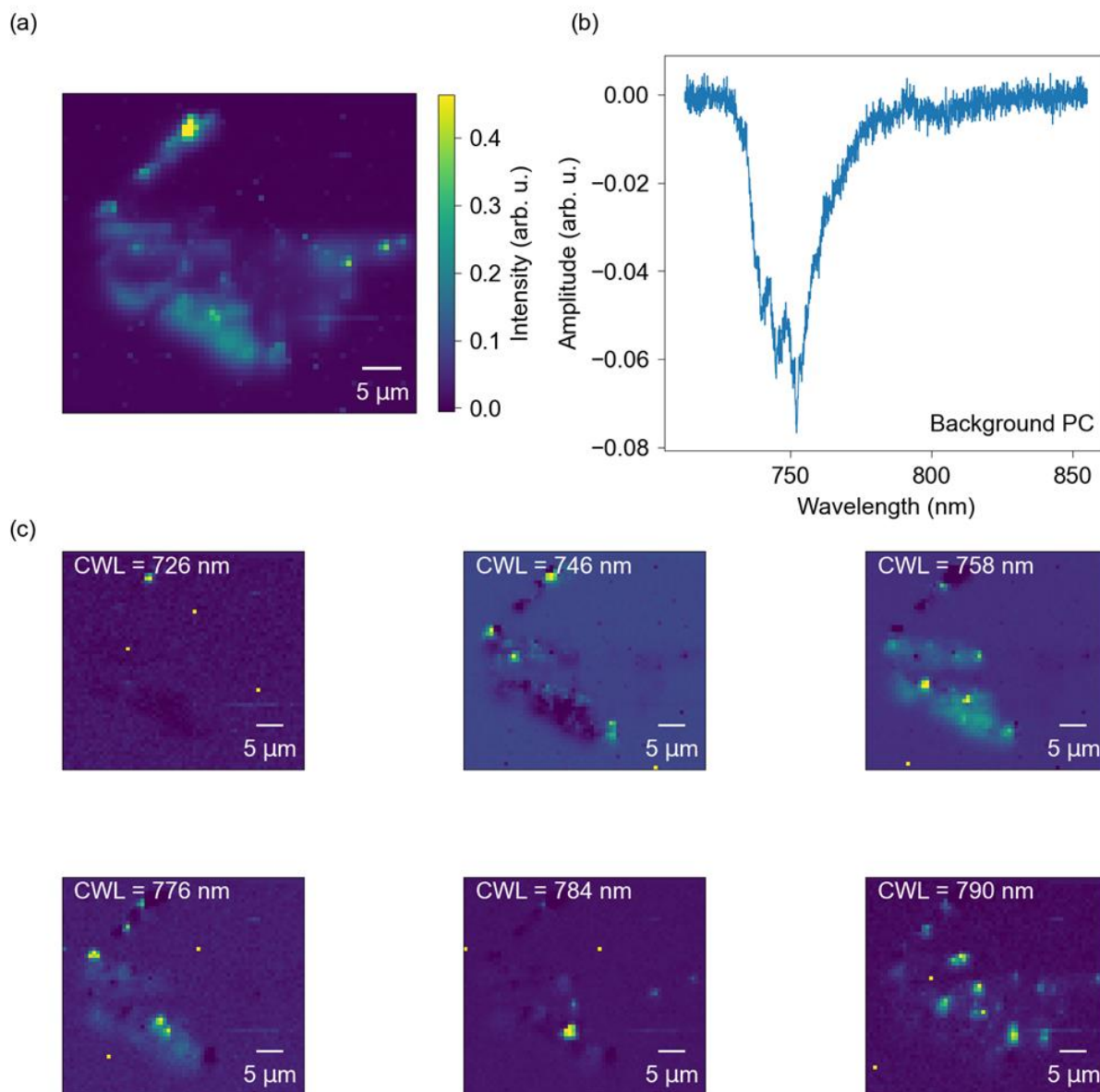


Figure S2 – Spatially localized photoluminescence from Samples 2 and 3. (a), integrated PL intensity map of the regions under investigation. (b) The principle component that was identified as the most significant contributor to spectrally broad PL emission. (c) A mosaic of the reconstructed hyperspectral map with the principle component in (b) removed. The intensity maps were generated by integrating the intensity of each spectra within a 2 nm band centered at the center wavelength (CWL) denoted on each map.

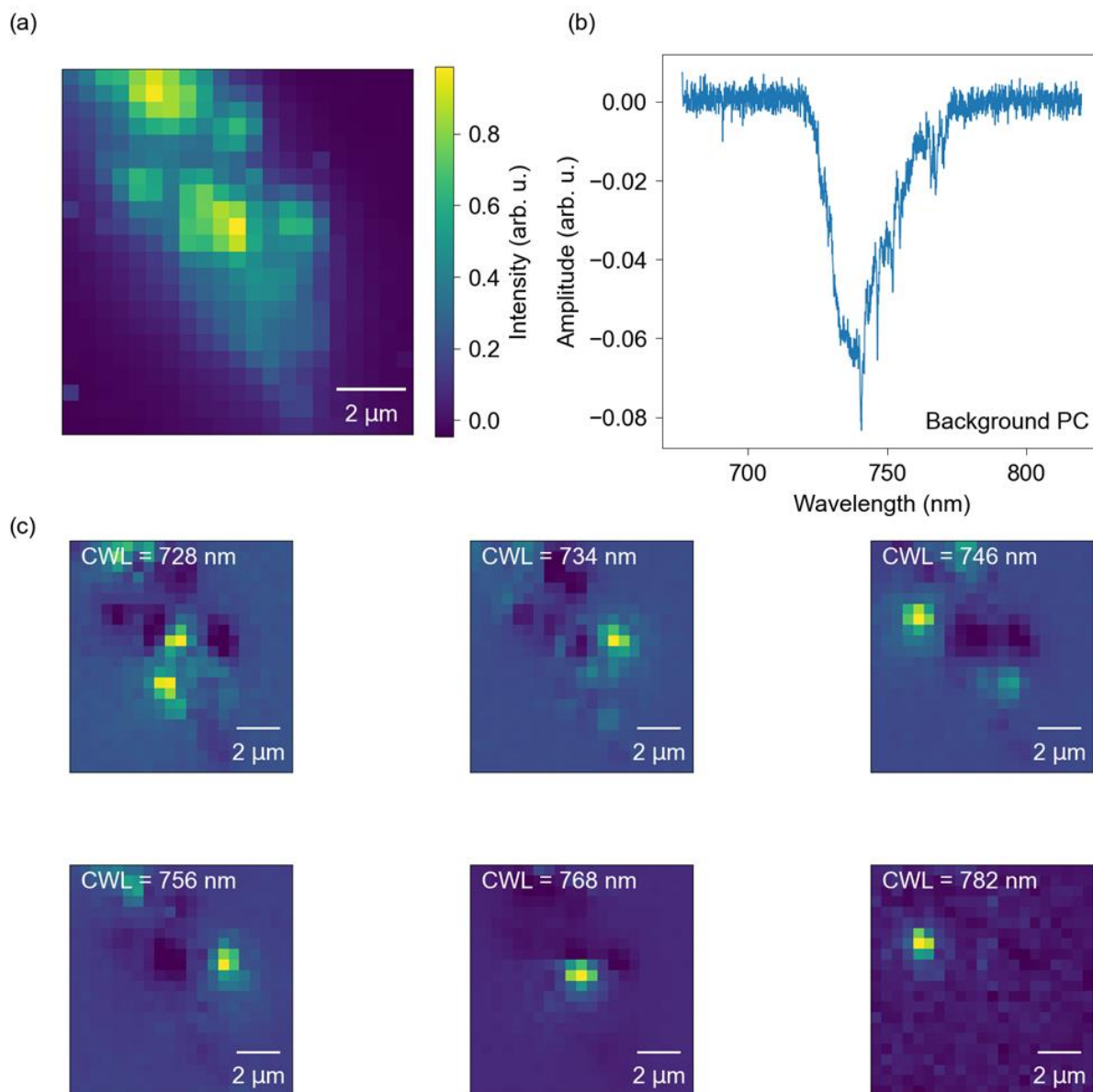


Figure S3 – Spatially localized photoluminescence from Sample 4. (a) Integrated PL intensity map of the regions under investigation. (b) The principle component that was identified as the most significant contributor to spectrally broad PL emission. (c) A mosaic of the reconstructed hyperspectral map with the principle component in (b) removed. The intensity maps were generated by integrating the intensity of each spectra within a 2 nm band centered at the center wavelength (CWL) denoted on each map.

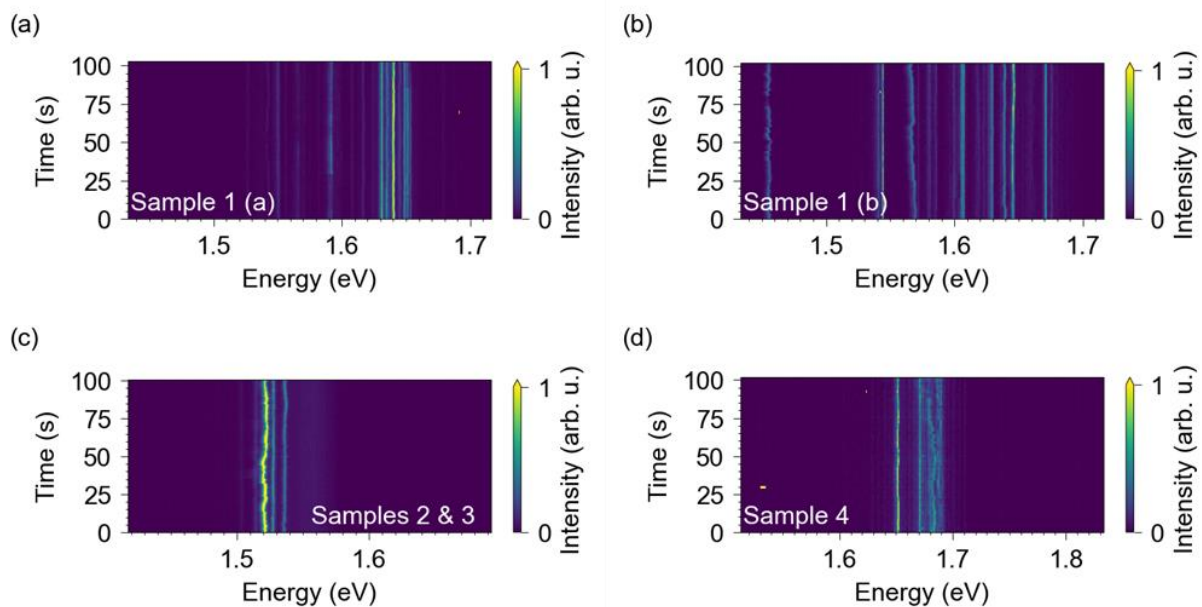


Figure S4 – Quantum emitter blinking and spectral diffusion. (a) & (b), Photoluminescence (PL) time series of two different locations on Sample 1. (c) PL time series from a location on Sample 2/3. Note – Both samples 2 and 3 exhibited QE blinking and spectral diffusion. (d) PL time series from a location on Sample 4.

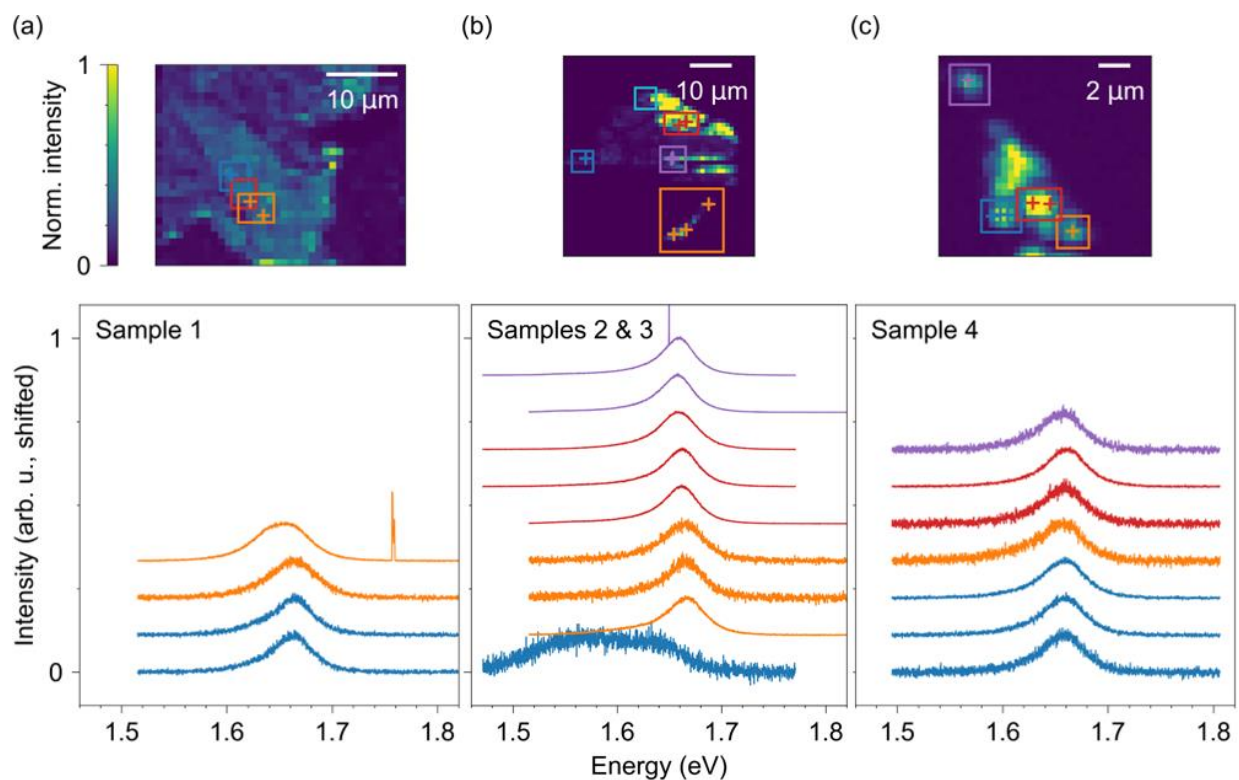


Figure S5 – Additional room temperature photoluminescence (PL) characterization. (a-c) top row, spatial maps of integrated PL intensity measured from each sample. Each color-coded region is at the same approximate location as in Figs. 1 & 3. (a-c) bottom row, PL spectra taken from the points denoted by the color-coded cross annotations in the maps.

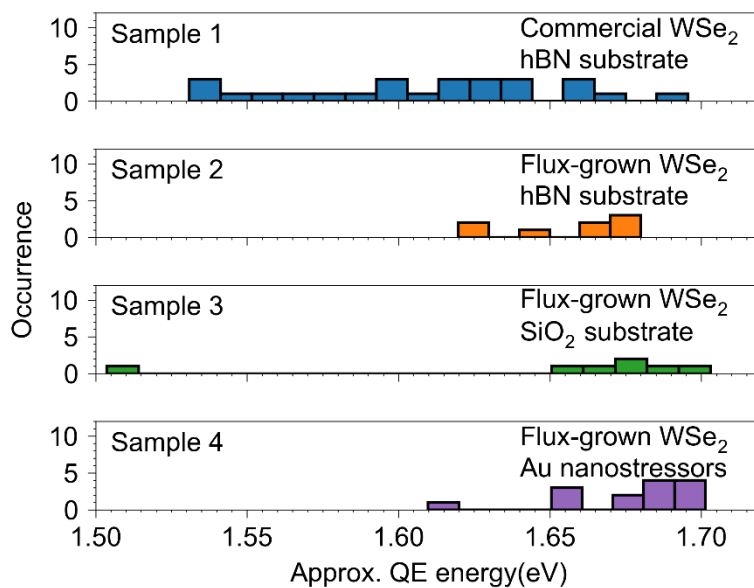


Figure S6 – The distribution of energies of the QEs measured. Sample 1 exhibits the broadest distribution and Sample 4 hosts the tightest distribution of QE energies.

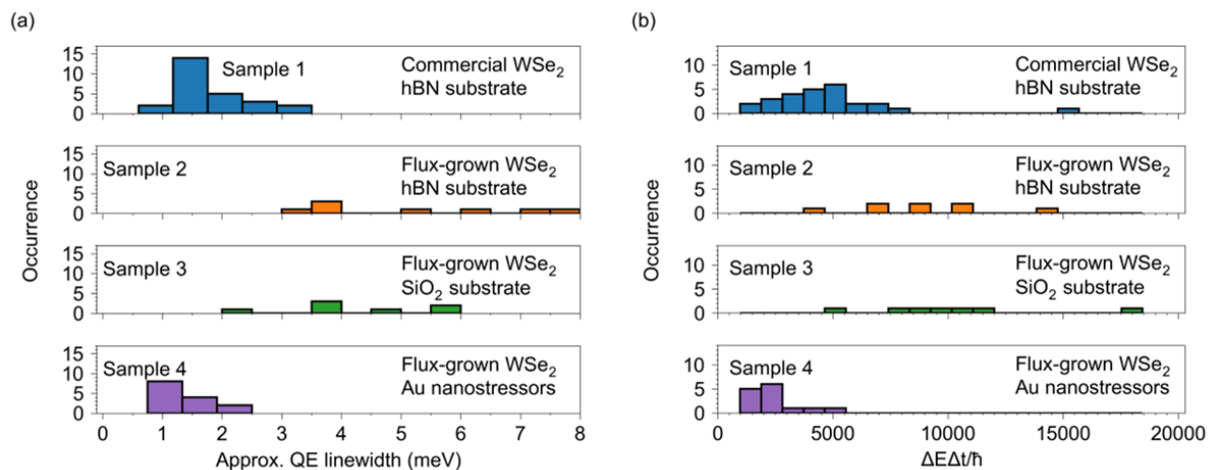


Figure S7 – Linewidth analysis of QEs. (a) The distribution of estimated linewidths of the QEs measured in this work. (b) The closeness of the emitters to the transform limit. ΔE is the linewidth of the QE and Δt is the characteristic linear decay time. Scaling the product $\Delta E \Delta t$ to the reduced plank constant, $\hbar$, yields an estimate of the deviation away from a transform limited linewidth and decay time.

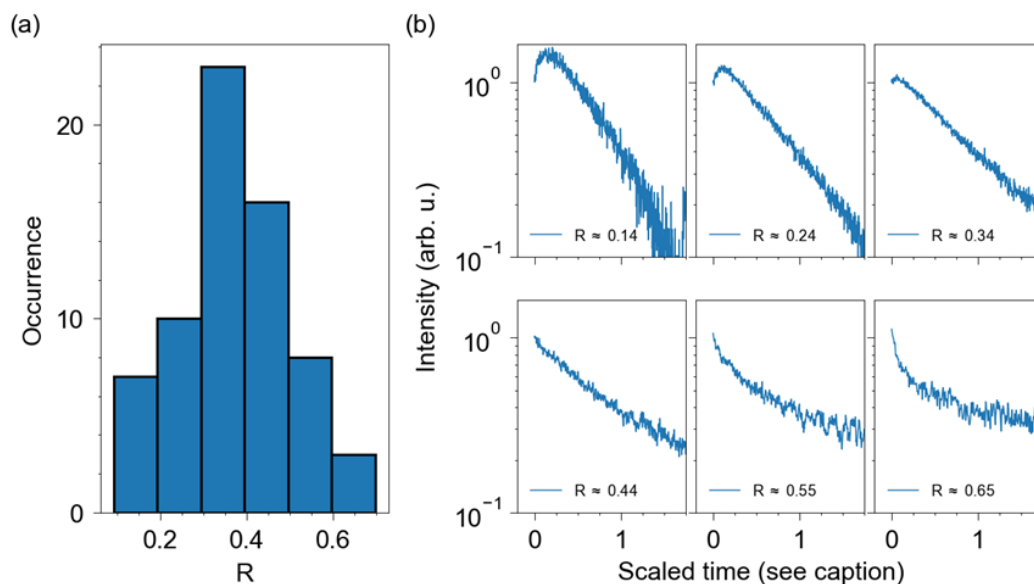


Figure S8 – Characterization of the intensity ratio metric, R . (a) Histogram of R for all PL time transients reported in this work. (b) The mean PL transient of each bin in (a). The time axis for each decay trace was scaled by the effective lifetime of the emitter before averaging. There is a clear shift from transients with delayed onsets, to monoexponential shapes, to biexponential shapes with increasing R .

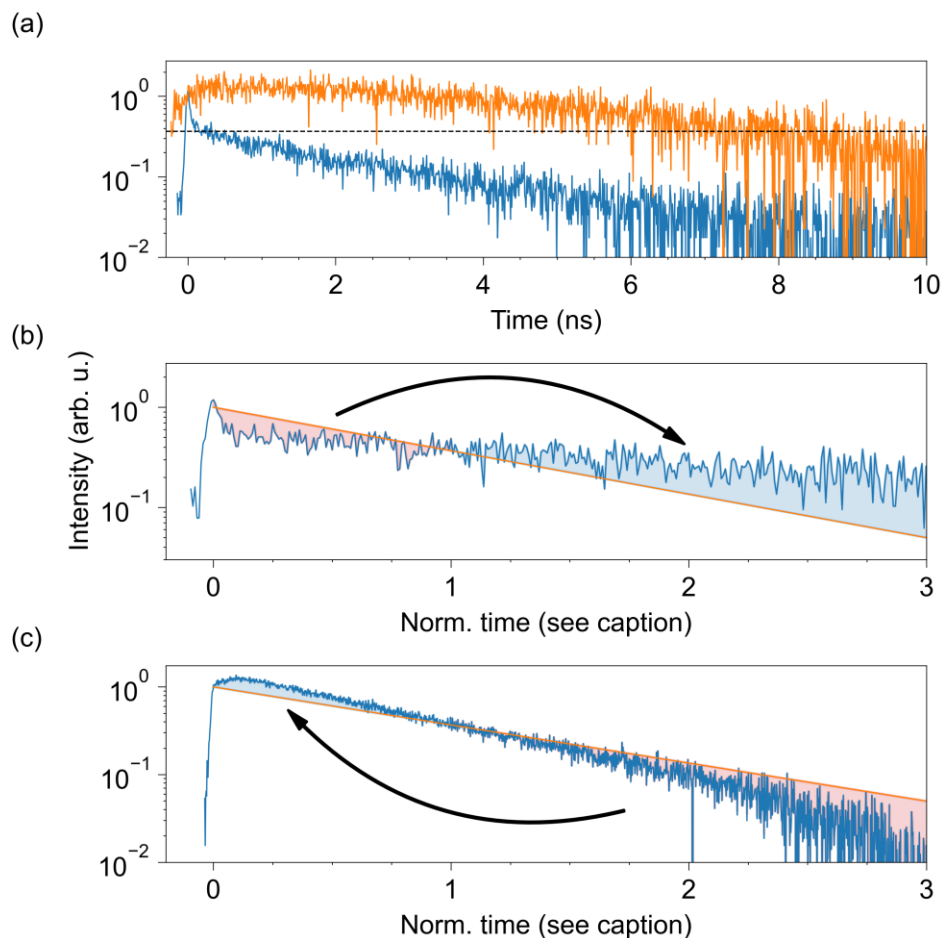


Figure S10 – Additional example photoluminescent transients that demonstrate the variety of kinetics measured. (a) Transients that exhibit a long effective lifetime ($\tau_{\text{eff}} \approx 8$ ns), orange, and a short effective lifetime ($\tau_{\text{eff}} \approx 0.36$ ns), blue. The horizontal dashed line is the threshold intensity level that defines the effective lifetime ($I/I_0 = e^{-1} \approx 0.36$). (b) A representative PL transient that exhibits strong biexponential decay characteristics (blue) and (c) a representative transient that exhibits a delayed onset characteristic (blue). The horizontal axes in (b) and (c) are scaled such that the effective lifetime of the emitters equals 1. Overlaid in orange in (b) and (c) is a single exponential function that has the same effective lifetime as the emitter. The shift of intensity relative to the single exponential function to longer (shorter) times is indicated by the colored shading and arrow annotations.

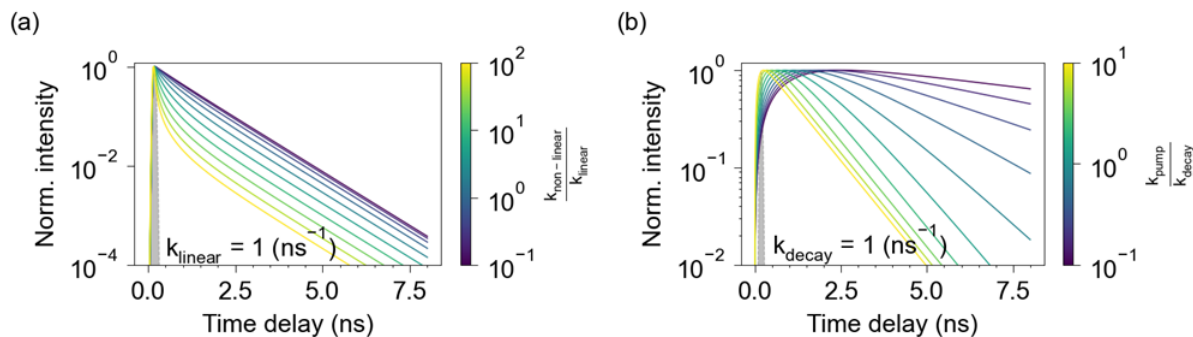


Figure S11 – Numerical simulations of excited state dynamics. (a) The evolution of the biexponential-like characteristic as a function of the strength of a nonlinear decay channel. (b) The evolution of the delayed-onset characteristic as a function of the rate at which a QE is pumped by a long-lived initial state.

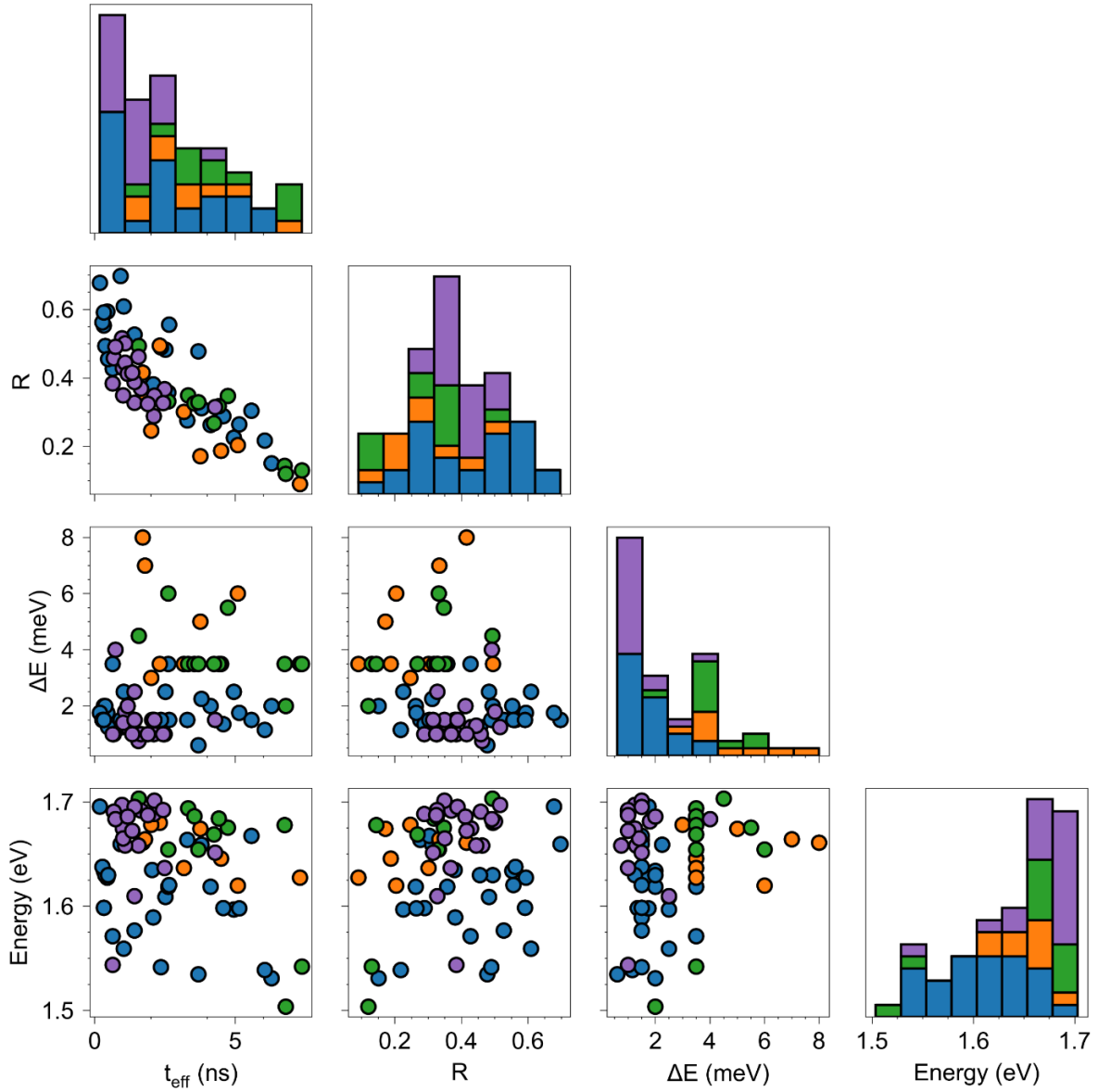


Figure S12 – Corner plots of the effective lifetime, shape metric, linewidth, and energy of each emitter reported in this work. Data for Sample 1 is plotted in blue, Sample 2 in orange, Sample 3 in green, and Sample 4 in purple.

CHAPTER 5

CHARACTERIZATION OF QUANTUM DOT-LIKE EMITTERS IN ARRAYS OF
NANOWRINKLES OF 1L-WSe₂Contribution of Authors and Co-Authors

Manuscript in Chapter 5

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Contributions: conducted AFM measurements of the samples, conducted the optical spectroscopy measurements and data analysis, wrote the manuscript.

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Contributions: fabricated the WSe₂ nanowrinkle array sample, conducted the optical spectroscopy measurements and data analysis, conducted initial spectroscopic characterization writing the manuscript.

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Contributions: writing the manuscript.

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Contributions: conceived this work, writing the manuscript.

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Contributions: conceived this work, writing the manuscript.

Manuscript Information

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Abstract

When combined with nanostructured substrates, two-dimensional semiconductors offer unprecedented potential to engineer strain and tailor light-matter interactions on the nanoscale. Recently, room-temperature nanoscale exciton localization with controllable wrinkling in 1L-WSe₂ was achieved using tailored arrays of gold nanocones. Here, initial characterization of the formation of quantum dot-like states and single-photon emitters in the 1L-WSe₂/nanocone system is reported. The nanocones induce a wide range of strains, and as a result, an ensemble of narrowband, potential single-photon emitters is observed that spans 200 meV in emission energies. Analysis of the distribution of emitter energies reveals that most reside in two spectrally isolated bands, leaving a less populated intermediate band of emitters that are spectrally isolated from the ensemble. The spectral isolation is advantageous for high-purity quantum light emitters, and anti-bunched emission from these states is confirmed. Emission polarization anisotropy is correlated with the nanoscale structure of the wrinkles, offering initial evidence that the orientation of the wrinkles influences the polarization of the emitter. Finally, the ensemble of quantum dot-like emitters in a given region is found to change with a thermal cycle from 4 K to 300 K and back to 4 K. The thermal-induced change highlights the need for these systems to control factors such as temperature-induced strain to enhance the robustness and repeatability. The initial characterization dataset highlights how controlled nanowrinkles of 1L-WSe₂ have the potential for generating quantum light sources with tailored polarizations in addition to uncovering potential challenges concerning thermal cycling that need to be overcome for technological applications.

Introduction

Solid-state quantum emitters (QEs) are essential for next-generation on-chip quantum photonic devices^{1,2}. Yet, there are significant challenges to overcome before realizing such systems. There are stringent requirements on nanoscale positioning, efficient photon outcoupling, high photon purity, and control over the polarization state of the emitted light. Over recent years, QEs in 2D semiconductors³⁻⁷ have emerged as a promising platform to realize such emitters^{5,8,9}. Their atomic thinness inherently overcomes the issue of inefficient outcoupling, makes them readily addressable both optically and electrically¹⁰, enables nanoscale positioning when coupled with precisely fabricated nano stressors¹¹, and facilitates novel functionalities such as highly-tunable strong coupling¹². Ongoing challenges with 2D QE platforms^{9, 13} include achieving room temperature operation, increasing photon purity, and increasing emitter indistinguishability^{1, 13}. These challenges motivate the exploration of new 2D emitter platforms that able to address these challenges.

A nearly ubiquitous feature of QEs in 2D semiconductors is their formation in regions of substantial material strain. Recent theoretical work¹⁴ has unified many experimental reports by proposing a model in which 1L-WSe₂ QEs form when strain lowers the energy of the conduction band enough to hybridize with defects within the band gap. Exciton funneling subsequently efficiently pumps the hybrid defect state. Motivated by these recent theoretical and experimental¹⁵ observations, we have fabricated samples consisting of high-quality monolayer (1L-) WSe₂ stressed by arrays of sharp gold nanocones. In previous work, we demonstrated control over the formation of nanoscale wrinkles in the 1L-WSe₂ sheet and observed that these wrinkles host localized excitons at room temperature¹⁶.

Here, we provide initial characterization of the localized quantum dot-like emitters that emerge in the controlled wrinkles generated by the arrays of gold nanocones. At cryogenic temperatures, a large ensemble of quantum dot-like states that spans 200 meV in emission energy is observed. Within this ensemble of emitters, two bands are highly populated with emitters. These two bands are separated by a spectrally dark region that is relatively sparsely populated with emitters, making it ideal for identifying and developing single-photon emitters with high photon purities. The emitters in all of these bands exhibit temperature-dependent fluctuations of intensity (i.e., blinking) and emission energy (i.e., spectral diffusion). By correlating cryogenic micro-photoluminescence hyperspectral imaging with room-temperature atomic force microscopy (AFM), a preliminary alignment of emitter polarization with the orientation direction of the underlying nano wrinkle is observed, highlighting the potential for tailoring emitter properties via wrinkle-engineering. For the spectrally isolated emitter, photon antibunching is confirmed and demonstrates that nanocone arrays generate QEs. However, the emitter states from the same region of the sample are shown to change when the sample temperature is cycled from 4 K to 300 K back to 4 K highlighting a potential technological challenge and the need to better understand how microscopic strain in all 2D semiconductor QE platforms changes with temperature. Overall, these studies offer initial insight into using engineered arrays of wrinkles of 1L-WSe₂ for solid-state quantum light sources and motivate future studies that exploit the controllability of the wrinkles to further unravel how strain, exciton localization, and exciton funneling combine to form single photon emitters in 2D materials.

Results

Figure 1a presents an AFM height map of the 1L-WSe₂ flake draped over the array of gold nanocone stressors. The fabrication of the sample follows the procedure described in a previous study¹⁶. The 1L-WSe₂ is forced to deform at each lattice site in the stressor array due to the prominence of the nanocones. There is a large variety of deformations observed that include conformal coverage of stressors, wrinkling between array sites, fine wrinkling near the apexes of the nanocones, and kinks where multiple wrinkles intersect or avoid crossing. The strain imparted to the 2D sheet by the stressor array and the corresponding room-temperature exciton properties in this system were systematically studied previously¹⁶.

To characterize the low-temperature optical properties of the 1L-WSe₂/nanocone system, we used a custom-built laser-scanning fluorescence microscope that is capable of hyperspectral photoluminescence (PL) imaging at variable temperatures down to 4 K. Hyperspectral maps of the photoluminescence from the sample are constructed by scanning the focused laser spot over the surface of the sample while recording the resulting PL emission spectrum, enabling simultaneous characterization of the spatial variabilities of the PL intensity and energy. Figure 1b shows a spatial map of the integrated PL intensity, which reveals substantial variations in the emission intensity over the extent of the flake. The spatial resolution of the hyperspectral PL measurement is ~700 nm, which limits the ability to search for direct correlations between emitters and the nanoscale structure of the sample. Nevertheless, it is apparent that the variations of the integrated intensity are not strongly correlated to the structure of the sample, even on relative coarse length scales. A pattern corresponding to the array of nanocones is not discernible in integrated intensity, and regions with and without extensive wrinkling exhibit bright and dim photoluminescence. This lack

of correlation indicates that 4 K photoluminescence depends on several competing factors that potentially include nanoscale strain¹⁷, Purcell enhancement^{18, 19}, and gold-induced quenching.

When the hyperspectral PL map is unpacked to reveal the spectroscopic data, an ensemble of sharp narrowband emitters appears (Figure 1c). These spectra are reminiscent of those previously reported by refs^{3-6, 20, 21} and are known to signify possible single-photon emitting states. To produce the waterfall plot shown in Figure 1c, we unpacked the hyperspectral map along a Hilbert curve²². In short, a Hilbert curve transforms the 2D coordinates of the hyperspectral scan into the vertical ordering of the spectra in the waterfall plot in a way that retains the 2D information of the map better than standard unpacking techniques (See SI note ##). As a result, neighboring points in the 2D hyperspectral map are plotted near each other in the waterfall plot. Using a Hilbert curve to unpack the hyperspectral map and order the waterfall plot allows us to more easily visually identify 2D spatial and spectral variability. In the spectra here, two main bands appear within the forest of narrow emission; a high energy band centered at approximately 1.675 eV and a low energy band centered at 1.55 eV. The intensity distributions of these bands are inhomogeneously distributed over the 1L-WSe₂ sample, as shown in Figures 1d and 1e. The low energy band tends to be concentrated towards the upper right of the flake whereas the high energy band is concentrated towards the lower left of the flake. There is also a spatially and spectrally isolated emitter that is nestled between the two main emissions bands at about 1.63 eV. Among the three bands observed, demonstration of photon-antibunching favors the isolated emitter in the middle band due to the relative ease in which a single emission band can be isolated. However, following reports of QEs in prior work, photon anti-bunching is expected from emitters in all three regions.

To gain deeper insight into any major difference emitters in the two different bands, we characterized their temporal fluctuations of the intensities and energies in Figure 2. Emitters from each of the three bands were simultaneously characterized by focusing on a region in the lower left region of the sample where PL from all three bands is present. The PL emission of the narrowband emitters is highly unstable at 4 K as seen in Figure 2a which shows the temporal evolution of the emitters in each band recorded over 4 minutes. The emitters in all three bands exhibit strong blinking and spectral diffusion. From this dataset, the intensity and spectral fluctuations for each band can be quantified with their integrated intensities and spectral medians, respectively. The histograms in Figures 2b-g and 2i-n report the distributions of the integrated intensities (Figure 2b) and spectral medians (Figure 2c) of the main branches of the PL spectrum (blue and red histograms) and the isolated emitter that is between the two bands (orange histograms). The intensities of each emission band are normally distributed at 4 K, which is consistent with the random blinking cycles commonly observed in semiconductor quantum dots^{23, 24} and previous reports of localized states in 2D materials^{6, 25}. The variance of the emission intensity of the high-energy band is nearly 2× that of low-energy band. The reduced intensity variance indicates that the low-energy band hosts systematically more stable emitters.

The distribution of emission energies for the spectrally isolated emitter in the middle band is skewed to lower energies while those of the upper and lower PL branches exhibit normal distributions. Similarly to the emission intensity, the variance of the emission energy of the high-energy band is approximately 1.8× that of the low-energy band, indicating that the low-energy band hosts more stable emitters. Our analysis here reports the average dynamics of the emitters within the band. Because individual emitters are unable to be tracked from one-time step to the

other, the statistics reported here for the upper and lower bands are ensemble averages. It remains unclear what the underlying mechanism of the blinking and spectral diffusion is. The observations here motivate further studies where more detailed analysis of the blinking and diffusion statistics collected over longer periods of time are compared with those of semiconductor quantum dots²⁶ to elucidate the underlying photo physics. These variations are simultaneously a strong indication that the emission features correspond to single QEs while posing challenges for characterization and stabilization.

Using these statistical descriptors, the intensity and spectral variations of the ensembles of emitters within the upper and lower branches stabilize near 50 K (Figure 2h-n). The variation in the integrated intensity due to blinking is reduced by about a factor of 2 upon warming to 50 K. In stark contrast, the spectrally isolated emitter in the middle band exhibits long off cycles with intermittent bursts of emission. The distributions of spectral medians follow a similar trend with increasing temperature. The distributions of the main low- and high-energy bands narrow (i.e. stabilize) while the spectrally isolated emitter retains its large skew towards lower energies. In contrast to these general trends, a close inspection of the colormap in Figure 2b reveals that there are random bursts of emission within the main branches, which is unresolved in our statistical analysis of the ensemble behavior of the bands. These random emission events within low- and high-energy bands suggest that there are emitters with dynamics like those of the spectrally isolated emitter.

Figure 3 further characterizes the linear polarization anisotropy of the PL emission in each of the three emission bands. Here, a linear analyzer was used in the detection path to determine the polarization states of the emitters. Figure 3a and Figure 3c show colormaps of the polarization

dependence of the PL emission intensity as the polarization analyzer was swept through two full rotations. Multiple rotations were done to measure the polarization anisotropy over the blinking and spectral diffusion cycles. The same data is plotted in both colormaps, but the saturation value in Figure 3c is lowered significantly to reveal emission features that are much dimmer than the dominant emission lines. Polar plots of the same data are inset in the main panels. Strikingly, a range of linear polarization anisotropies are observed. Figure 3b shows that the high-energy band (solid blue) and the spectrally isolated emitter (solid orange) are both strongly linearly polarized, but exhibit different orientations of transition dipoles. The low-energy band is significantly less polarized, only slightly favoring a linearly polarized state that is distinct from the high-energy and spectrally isolated emitter. In Figure 3c, the polarization anisotropies of two of the substantially more dim emitters are analyzed. One emitter (red) is 20 meV higher in energy than the high-energy band and the other emitter (blue) is 20 meV higher in energy than the low-energy band. Figure 3d shows that both emitters exhibit linear polarization anisotropy with a preferential polarization state that is orthogonal to the bands of which they neighbor. For instance, the emitter that is 20 meV higher in energy than the high-energy band is polarized at ~ 50 degrees while the low-energy band is polarized at ~ 140 degrees. If the cross-polarized emitters originate from the same set of states, the large splitting between them is suggestive that the zero-field splitting of these emitters is increased in the presence of large uniaxial strain. The significant difference in the PL intensities of the cross-polarized emitters is then congruent with thermal effects leading to a preferential occupation of the lower energy bands.

Of the ensemble of emitters observed in this system, the emitter that is spectrally isolated is the most promising state for generating single photons. The spectrally isolated nature of its

emission naturally promotes emitter purity without the need for excessive emission filtering. Figure 4a presents a representative PL spectrum taken from the region in the lower left area of the flake where the emitter is localized. The left inset shows the time-resolved PL of the emitter. We spectrally discriminate the PL emission by using a monochromator exit port on our grating spectrometer. The spectrally filtered light is then relayed onto a single-photon avalanche photodiode and a histogram of detection events is constructed relative to pulsed laser excitation. Using this technique, the excited lifetime of the emitter is measured to be approximately 5 ns, which as reported in previous studies may convolve a wide range of dynamic processes (c.f. Chapter 4).

In addition, the temperature dependence of the second-order intensity correlation function ($g_2(\tau)$) of this emitter was also measured with a Hanbury-Brown-Twiss (HBT) interferometer. At zero-time delay, we observe strong suppression of the coincident count rate at 4 K (the blue trace in the right inset), signifying photon antibunching. The suppression of the coincident count rate is unambiguous evidence that the spectrally isolated emitter is a quantum emitter (QE; i.e., emits single photons). We also measured $g_2(\tau)$ at 25 K (orange) and 50 K (red). At these elevated temperatures, the antibunching dip persists but the contrast with the neighboring peaks of the pulse train is significantly reduced. We believe that this is due to the long “off” cycles that develop at elevated temperatures (c.f. Figure 2b) which results in a dramatic decrease in the average emitter count rate.

Figure 4b shows the PL intensity integrated within a small spectral band centered on the emission of the isolated emitter. The precise limits of the spectral band are shown by the shaded region underneath the PL spectrum in Figure 4a. Overlaid on the filtered intensity map is the best

estimate of the location of the flake. The PL map and AFM were registered by using wide field-of-view PL intensity maps and large area AFM height maps. The homography between the two datasets was then calculated after manually identifying the location of features that appeared in both datasets²⁷. Using this method, we estimate that we have aligned the AFM data to the hyperspectral PL map near the spatial resolution of the PL scan.

With the aligned dataset, an initial correspondence between the observed quantum emitter and local deformation and strain in the 1L-WSe₂ can be established. The local strain of the 1L-WSe₂ is estimated by numerically calculating the curvature of the sheet, as shown in Figure 4c. The curvature was calculated by numerically differentiating the AFM height map presented in Figure 1a twice and serves as an approximate metric for the identification of locations where the 2D sheet is locally deformed. Although the curvature provides insight into the local deformations of the 1L-WSe₂, it is not necessarily directly proportional to the strain in the 1L-WSe₂. Prior work has shown that accurate modeling of strained 2D materials requires atomistic simulations^{12, 17, 28} of the 1L-WSe₂ lattice in regions of intense deformation. Here, we anticipate that the final version of this manuscript will include a strain simulation that utilizes elastic plate theory to estimate the strain given the nanoscale topography of the 2D sheet.

Figure 4d overlays the intensity of the PL emission of the antibunched emitter onto the spatial map of the topographic curvature. Here, the PL intensities are shown as contours whose color corresponds to an intensity level in the color bar of Figure 4c. Two wrinkles intersect near an Au nano stressor in the region where the PL emission of the isolated emitter originates. The angular offset between these two wrinkles is approximately 35 degrees. Notably, this offset corresponds to the total angular offset between the linearly polarized PL emission from the upper

and lower branches in the PL. We preliminarily hypothesize that the PL emission from the upper and lower branches may originate from the two main wrinkles while the isolated emitter is located at the intersection of the two wrinkles. This observation motivates future correlative studies that combined low-temperature PL imaging and spectroscopy, nano-optical imaging of localized states^{12, 17, 28}, and controlled wrinkle formation using different stressor arrays¹⁶.

Finally, Figure 5 shows evidence that emitter formation can be quasi-permanently altered by heating the sample from 4 K to 300 K. Following the characterization of the quantum emitter in Figure 4, the temperature of the sample was raised from 4 K to 300 K. The sample was warmed to 300 K by heating the sample stage while maintaining the high vacuum in the cryostat. The heater was subsequently turned off and the sample was cooled back to 4 K. Prior to the warm-up, emission from the QE was confirmed and it did not show any signs of photodegradation nor bleaching. Figure 5a compares the PL spectrum at 4 K before the warm-up, the PL spectrum of the same region at 300 K, and the PL spectrum of the emitter region at 4 K after a subsequent cool-down. The original 4 K spectrum (blue curve) shows strong emission from the QE at about 1.62 eV. After returning to 4 K, we were unable to locate the antibunched emitter. To account for microscope drift and emitter blinking, a hyperspectral map (unraveled and plotted in Figure 5b) and a time series of the PL (Figure 5c) were acquired to confirm that the emitter was no longer present after the temperature cycle. This initial observation reveals that QE formation in 2D materials may vary on each temperature cycle, which could be due to cooling-induced strain in the system. Such variability necessitates further investigation and motivates further refinement of temperature-independent strain generation in these systems.

Discussion

The origin of the emission lines is an outstanding question. From the spectral signatures observed here, the upper and lower bands of the PL likely arise from the hybridization of strained excitons with the two defect levels associated with a single selenium vacancy (V_{Se}) in the presence of strain, as is well-established in many other 1L-WSe₂ QE platforms. The energetic splitting between the high- and low-energy bands is ~ 125 meV and coincides with the expected splitting between the two in-gap states associated with a single selenium vacancy (V_{Se}) under strain^{15, 29}, which are anticipated to be the dominant crystal defect in the high-quality, flux-grown 1L-WSe₂³⁰ used here. Alternatively, the two upper and lower branches in the PL might be hybrid exciton-plasmon states (i.e., upper and lower polariton branches)³¹. In this case, we hypothesize that the localized surface plasmons at the apexes of the gold nanocone stressors are strongly coupled to the localized exciton states hosted in the neighboring 1L-WSe₂ wrinkles. Nevertheless, and independent of the branching mechanism, significant nanoscale variability in the magnitude and orientation of strain and the distance of the wrinkles from the Au cones is expected in this sample. This variability makes interpreting the far-field PL challenging.

In the model of strain-induced hybridization, the activation of bright emission from the defect levels depends sensitively on the energy of the conduction band edge through strain^{15, 32}. Due to the substantial variety of nanoscale deformation in this sample, we anticipate that the conduction band edge is swept nearly continuously through the defect levels across the spatial extent of the sample. Further, in Figure S2 of the supporting information, we identify two pairs of doublets within each emission band, which is indicative of an additional level of hybridization that leads to the additional fine structure in the PL. The spectrally isolated emitter studied here might

simply be the lowest energy doublet in the upper emission band and activated by a specific level of strain at that particular location on the sample.

The correspondence between the polarization angle of the PL and the orientation of the wrinkles offers a hint that the axis at which uniaxial strain is applied determines the polarization angle of the PL emission, reminiscent of how uniaxial strain rotates the valley pseudospin of bright excitons³³⁻³⁶. Finally, the energy of the dim cross-polarized emitters observed in Figure 3b also places an upper bound on the magnitude of the zero-field splitting of about 20 meV. We suspect that the emission intensity from the high energy state of the doublets is reduced due to the large splitting and thermal effects.

In conclusion, we report the emergence of a new class of low-temperature 2D QEs; 1L-WSe₂ nano wrinkle arrays. We observe that emitters in this system blink and spectrally diffuse, which poses technical challenges for characterization and device applications, that the polarization state of the emission corresponds to the direction of uniaxial deformation, and that the emitters are sensitive to thermal cycling.

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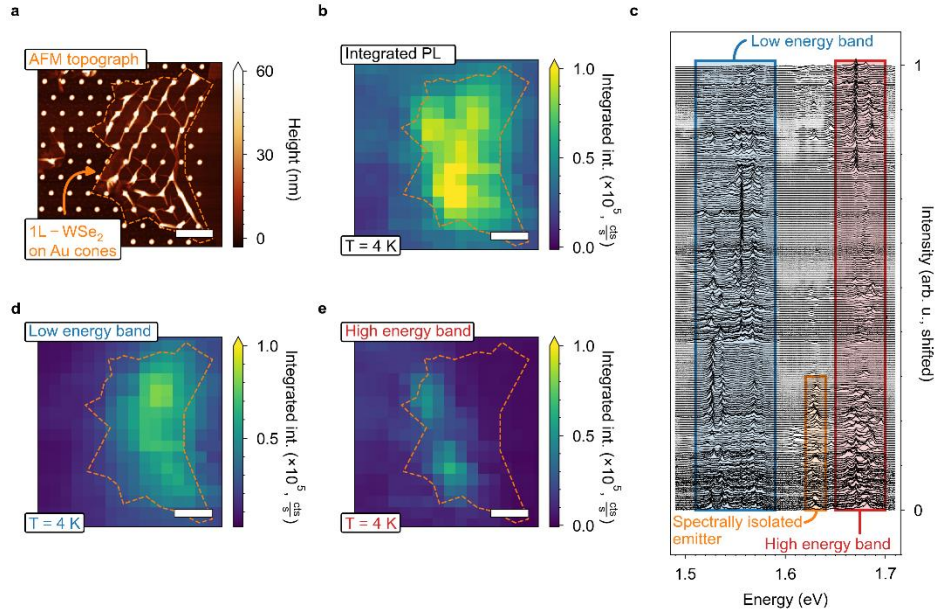


Figure 1 – Spatial and spectral inhomogeneity of the 1L-WSe₂ nanowrinkle array sample. (a) The nanoscale topography of the sample. (b) A spatial map of the integrated photoluminescence intensity. (c) A waterfall plot of the PL spectra unpacked from a hyperspectral map of the sample. (d) and (e), Maps of the PL intensity integrated within the low-energy and high-energy bands denoted in (c).

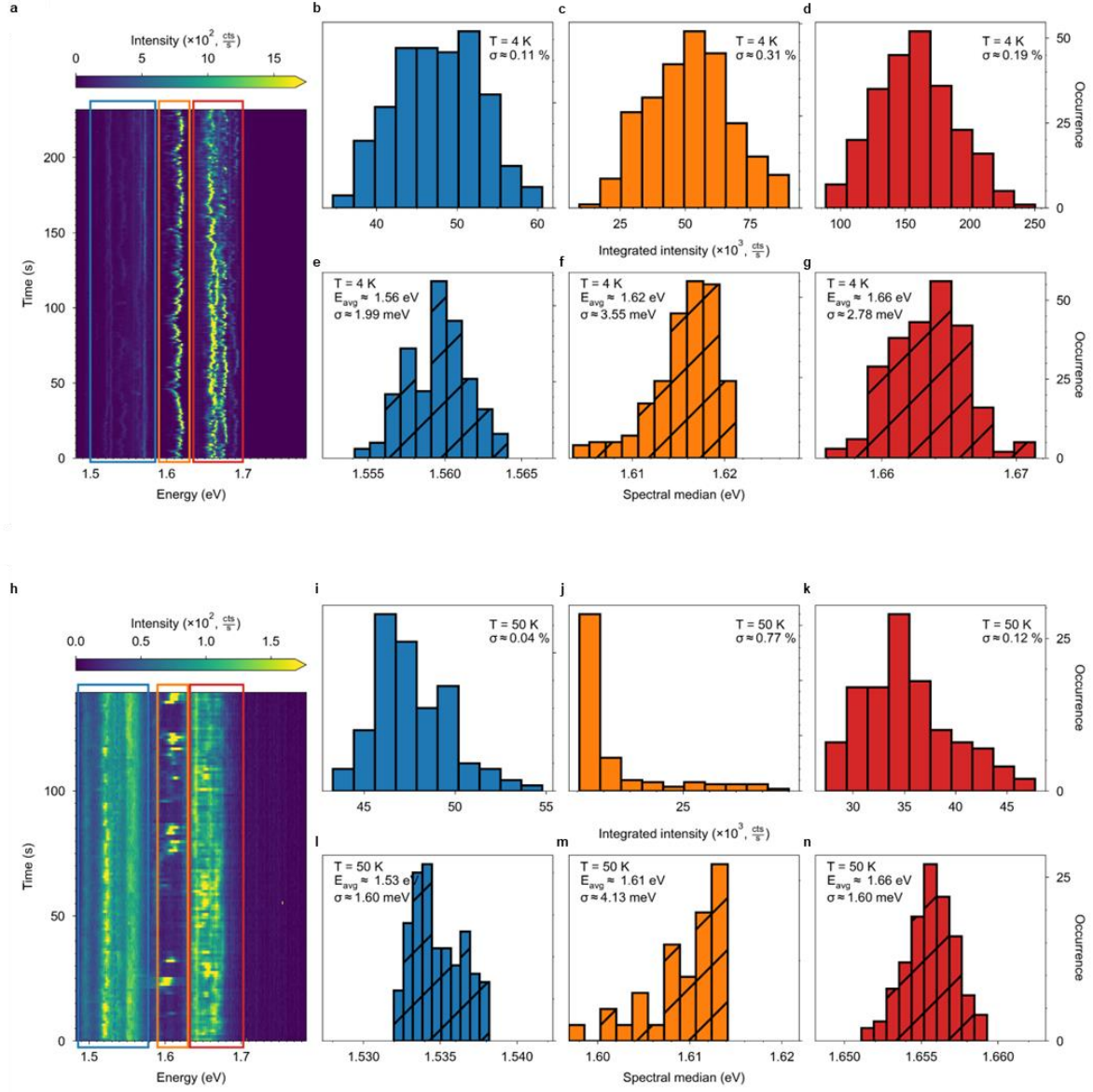


Figure 2- Variations in the emission intensity and energy of localized excitons. (a) and (h) Time dependence of the PL spectra at 4 K (a) and 50 K (b). The colored box annotations denote the bands in which the emitter intensities and emission energies are calculated. (b-d) The distribution of PL intensity over time within the low energy band (b), the spectrally isolated emitter (c), and the high energy band (d). (e-f) The median emission energy within each band. (i-k) the emission intensity within each band at 50 K. (l-n) The emission energy within each band at 50 K.

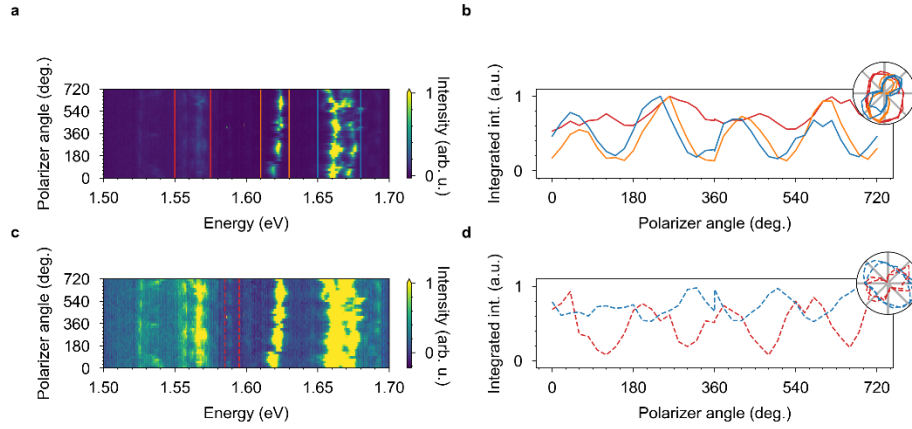


Figure 3 – Polarization anisotropy of localized emitters. (a) Linearly polarization dependence of the PL emission. (b) The integrated intensity of the polarized PL emission within each of the bands that are annotated in (a). Inset is a polar plot of the integrated PL emission intensity. (c), The same data as in (a) but with the saturation value is lowered to show dim and cross-polarized emission. (d) The integrated intensity of the polarized PL emission within each of the bands is annotated in (c).

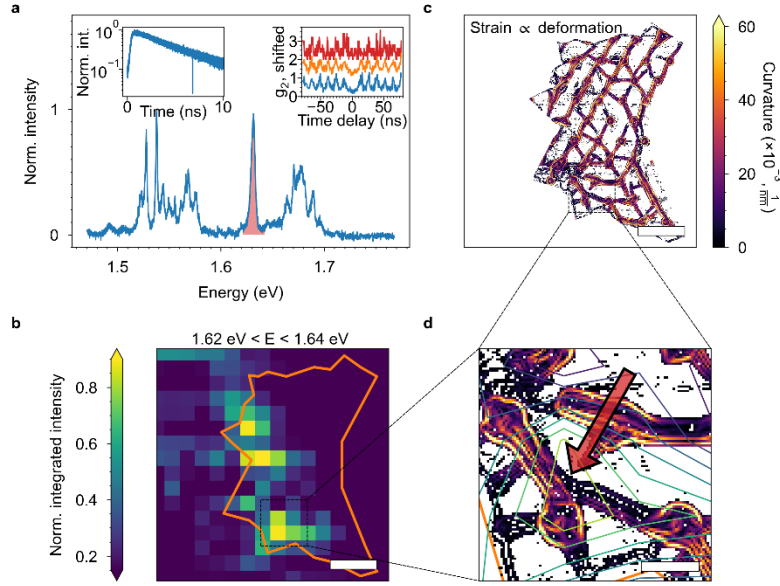


Figure 4 – Time-resolved emission properties and structural correlation of the spectrally isolated emitter. (a) An emission spectrum that shows intense PL emission from the isolated emitter. Time-resolved PL is inset (left) showing that the emitter has an excited-state lifetime of approximately 5 ns. The right inset shows the temperature dependence of the second-order intensity correlation function, $g_2(\tau)$, of the emitter; blue is measured at 4 K, orange is measured at 25 K, and red is measured at 50 K. (c) The curvature of the 1L-WSe2 wrinkle array. (b) The intensity distribution of the PL emission integrated within the spectral region of the isolated emitter in (a). (d) The PL intensity map in (b) is shown in the contours and registered with the curvature in (c). The PL emission from the spectrally isolated emitter emanates from the location marked by the red arrow, where two wrinkles intersect.

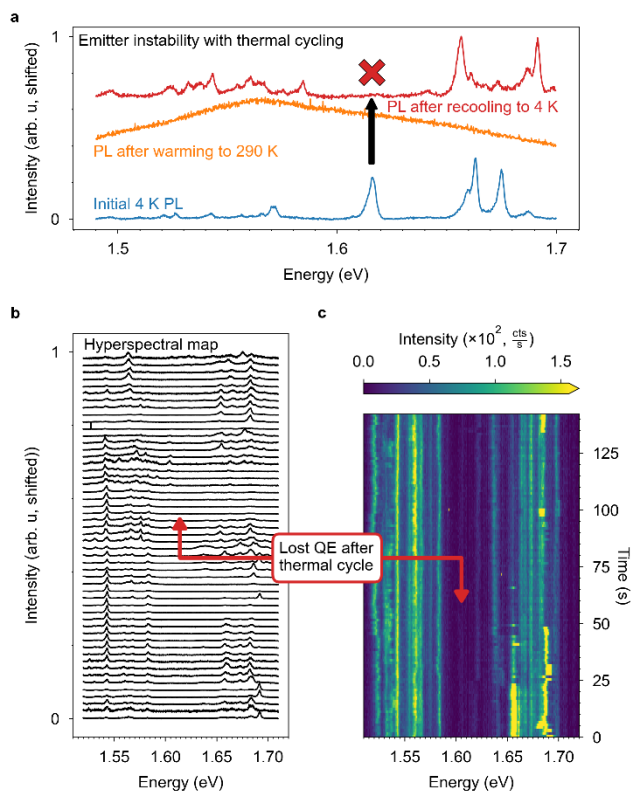


Figure 5 – Sensitivity of the emitters to heating. (a) The evolution of the PL spectrum as the sample was heated from 4 K (blue) to 290 K (orange) and cooled back to 4 K (red). The spectrally isolated emitter was not observed after the temperature cycle. (b) An unpacked hyperspectral map and (c) and PL time series showing the absence of the emitter.

Supporting Information: Characterization of Quantum Dot-Like Emitters in Arrays of
Nanowrinkles of 1L-WSe₂

Note 1: Using Hilbert Curves to Unpack Hyperspectral
Maps.

Hilbert curves provide a useful way to map 2D space onto 1D space while preserving the locality between points in 2D. Simply, the Hilbert curve wraps around itself as it tiles 2D space in a way that standard unpacking techniques do not. Consequently, using Hilbert Curves to determine the order that hyperspectral maps are unpacked aids in the visual identification of local spatial correlations. Figure S1 compares the waterfall plots generated from a standard “snake” unpacking order (where the spectra are unpacked in order along one dimension before stepping to the next point in the other dimension) versus using a Hilbert curve. The respective paths are overlaid on a map of the integrated PL intensity (Figure S1a and S1c) and the spectra in the waterfall plots (Figure S1b and S1d) are colored to correspond to the location that they were measured along the respective unpacking path.

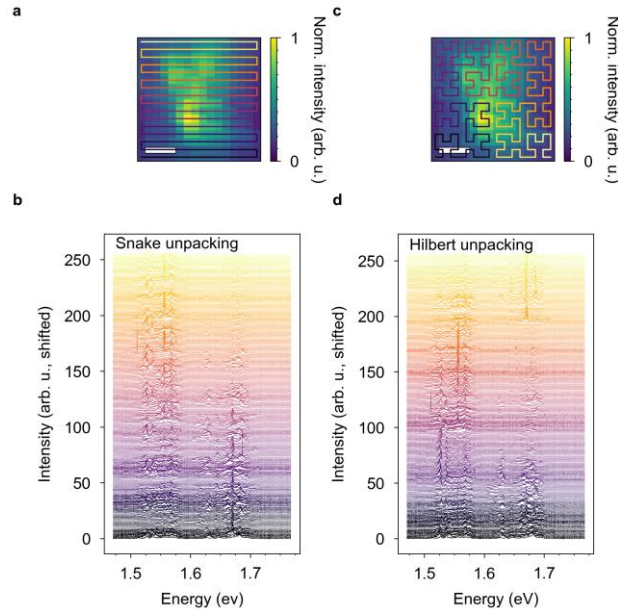


Figure S1 – Comparison of the waterfall plots produced from a hyperspectral PL map by using standard “snake” unpacking versus unpacking the map along a Hilbert curve. (a) and (c) the paths taken by the snake and Hilbert curves, respectively. (b) and (d), the corresponding waterfall plots. The spectra are colored to correspond to the points along the unpacking curve.

Note 2: Spatial Distribution of the Doublet Structure in the PL Emission.

Four doublets are observed in the 4 K PL spectra in addition to the main low- and high-energy branches that are identified in the main text. Figure S2a shows an unpacked hyperspectral map with the energies of the doublets marked by the solid lines. The energetic splitting in each doublet is approximately 10 – 12 meV. The PL intensity is integrated within a small band centered on each emission feature to produce the spatial maps in the mosaic on in Figure S2b.

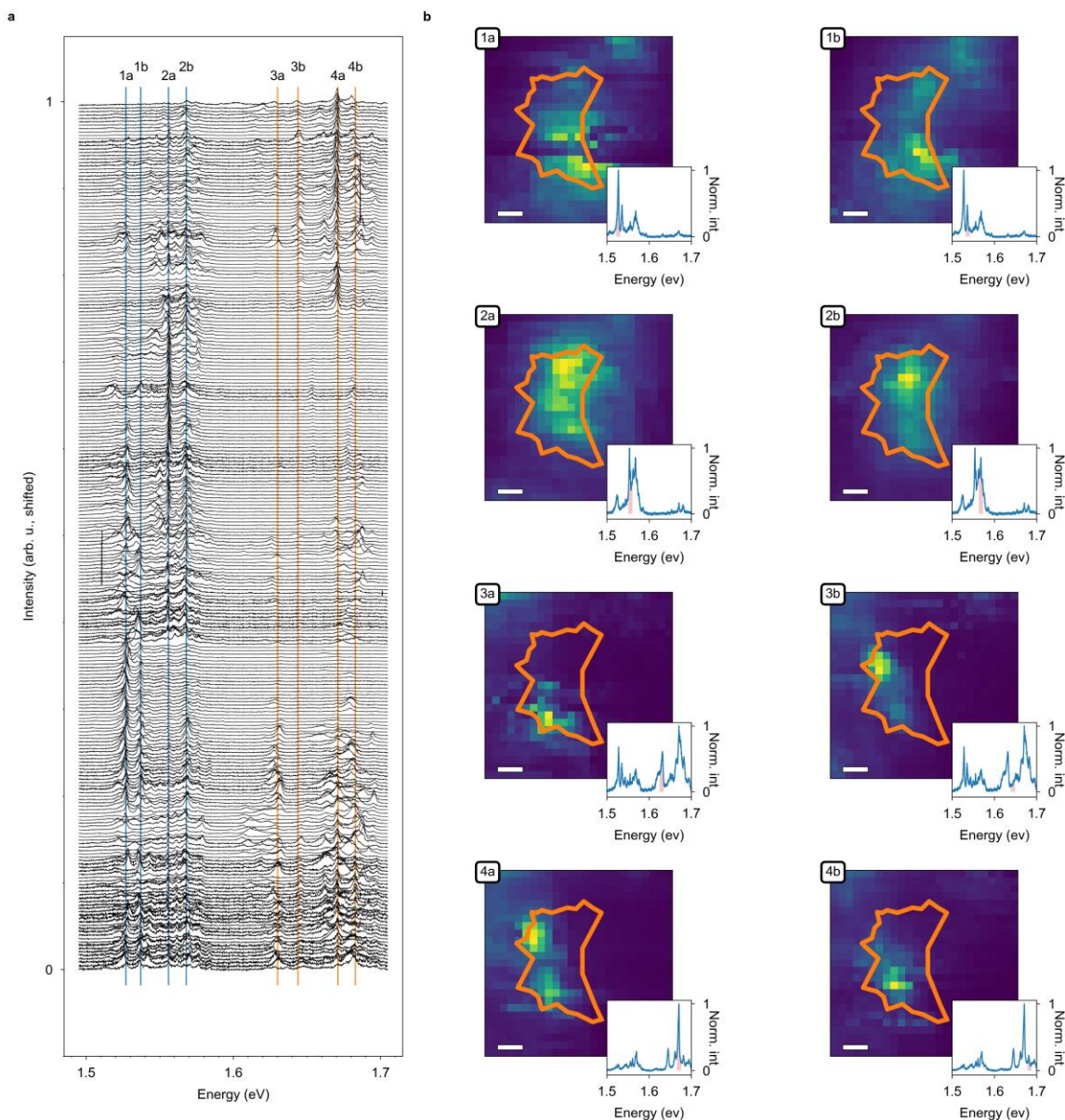


Figure S2 – Spectral identification of doublets in the PL spectra and their spatial distribution across the sample. (a) An unpacked hyperspectral map. The vertical lines are guides to the eye used to identify the emission energies of the doublets. Blue lines lie within the low-energy and identified in the main text and orange lines lie within the high-energy band. (b) A mosaic of the PL emission intensity integrated within a narrowband centered on the vertical lines overlaid on the spectra. The integration bands are shown in red on the PL spectra that are inset in the mosaic. The border of the 1L-WSe₂ flake is overlaid in orange. Scale bars are 1 μm .

Note 3: Spatial Registration of the AFM Topograph and the PL Intensity Maps.

AFM topographs and PL intensity maps were aligned using manual feature identification and subsequent image stitching by finding the homography between the two datasets. Figure S3a shows a composite AFM topograph that was stitched by manually aligning multiple scans. Figure S3b shows a PL intensity map taken over a large extent of the sample. The sample consists of the many small 1L-WSe₂ flakes that fractured during the transfer processes. These small flakes are identifiable in both the AFM and PL data, making them instrumental in the image registration process. The connecting markers between AFM and PL data show the location of the features that were used to calculate the homography between the two datasets. In brief, homography is a linear mapping (tilts, translations, rotations, stretching, etc.) between two planes. Particularly useful here is the ability of the capability to register these two datasets while accounting for any distortions in the PL or AFM maps that simple translations and stretching may not account for. Figure S3c shows an overlay of the registered images. The high-resolution hyperspectral image used in the main text is then manually registered to the PL map in Figure S3b to provide the final alignment between the topography and PL shown in the main text (c.f. Figure 4).

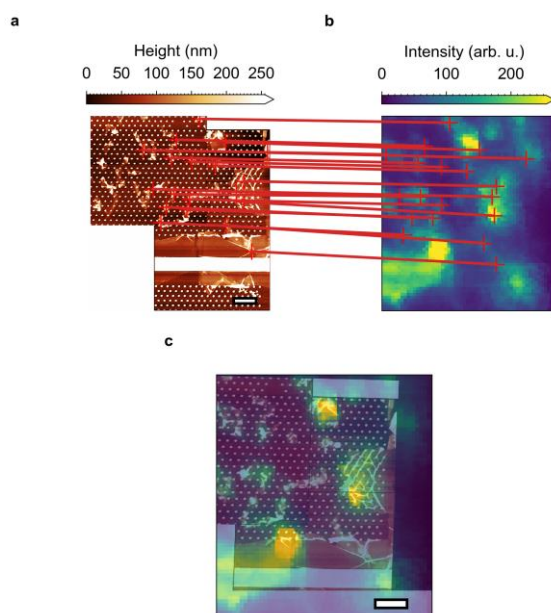


Figure S3 – Spatial registration of the AFM topograph and the PL intensity maps. (a) A mosaic of AFM topographs that are stitched together. (b) A wide-field PL intensity scan. Common features in (a) and (b) that are used to calculate the homography between the two images are marked by the red crosses and connected with lines. (c) An overlay of the registered images.

CHAPTER 6

CONCLUDING REMARKS

6.1 Summary

As with many scientific endeavors, the work here began with a different objective than what was ultimately accomplished. We set out to identify localized biexcitons in strained 2D semiconductors and harness them for quantum light emission. But shortly after we began this work, we discovered the enhancement effect of the unlocalized biexcitons reported in Chapter 3. That discovery sent us down an intricate path of thermalization and many-body physics that culminated with the modified PLE measurement used to quantify the increase in the biexciton quantum yield as the excitation energy is increased.

In parallel, our collaborators at Columbia University developed the 1L-WSe₂ wrinkle array samples. We noticed that the excited state lifetimes of the localized excitons in the wrinkle arrays were different from those of other 2D QE platforms. This discovery led to the development of the simple metrics used in Chapter 4 for cross-platform differentiation of QE population dynamics. Finally, the observation of single-photon emission from a wrinkle array sample led to the characterization paper in Chapter 5.

In summary, the work conducted in this thesis shows that the quantum yield of charged excitons and charged biexcitons increases with increasing photoexcitation energy in 1L-WSe₂ at 4 K, that 1L-WSe₂ wrinkle arrays are viable 2D quantum emitter (QE) platforms, and that the excited-state dynamics of the QEs hosted in the wrinkle arrays are accelerated and linearized compared to other 2D QE systems. More generally, this work contributes to the body of knowledge

of thermalization in materials with strong coulomb interactions and the origins and dynamics of 2D quantum emitters. I have developed a quantitative photoluminescence excitation spectroscopy technique to measure the quantum yield of non-linear excitons and have used novel statistical analysis to benchmark the dynamics of 2D QEs.

6.2 Future Directions

Improvements to the PLE Technique

The accuracy of the excitation spectroscopy technique developed in Chapter 3 is limited by the accuracy of the photoexcitation external quantum efficiency (EQE) calibration. As it stands, the EQE calibration relies on electromagnetic modeling of the sample using a dielectric function for 1L-WSe₂ at 4 K extracted from literature. A clear limitation in the work presented in Chapter 3 is the uncertainty of the dielectric function for 1L-WSe₂ at 4 K due to differences in the sample quality and supporting substrate. Thus, a way to improve the excitation spectroscopy is to develop an accurate measurement of the 4 K dielectric function of the exact sample under investigation.

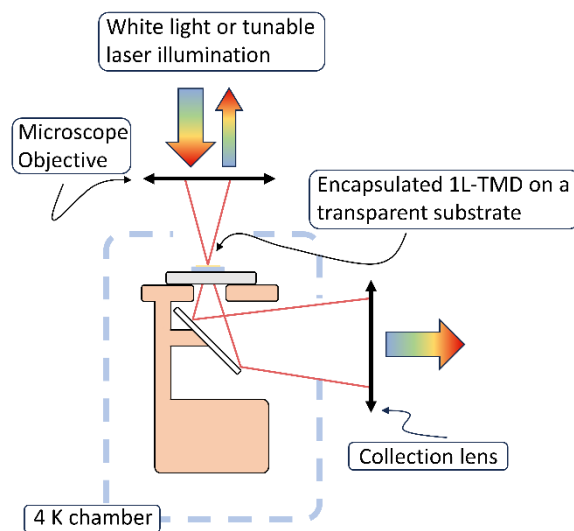


Figure 6.1 – Proposed experimental setup to measure the dielectric function of 1L-TMD semiconductors that are fully encapsulated in hBN. The sample is supported by a transparent substrate and mounted on a stage with an aperture. Light is focused onto the sample from above by a microscope objective. The reflected light is collected by the objective and routed to a detector array. The light that is transmitted through the sample is deflected by a turning mirror below the sample mount and collimated by a collection lens. The collimated transmitted light is then routed to the detector array.

To that end, the dielectric function can be more accurately measured by utilizing a transparent substrate and conducting both reflectance and transmission spectroscopy¹. A schematic of the experimental setup is shown in Figure 6.1. In essence, we would measure the differential reflection and transmission spectrum of the stack and deduce the complex dielectric function from the combined dataset without the need for Kramers-Kronig analysis. More generally, accurate dielectric functions of 2D TMDs encapsulated in hBN and at low temperatures are lacking¹⁻³. So, it might be worthwhile to conduct a systematic study that reports the dielectric function of 1L-TMDs encapsulated in hBN at low temperatures.

Exotic PLE Techniques

As shown in Chapters 2 and 3, photoluminescence excitation spectroscopy (PLE) inherently probes both the complex relaxation channels from a photoexcited initial state and thermalization processes in semiconductors. PLE is typically used to measure the transition energies of absorption resonance in 2D materials⁴⁻⁷. Slightly more advanced, PLE can be used to find the ideal energy to resonantly excite QEs and minimize decoherence processes⁸. But beyond these use cases, the work done in Chapter 3 demonstrates that using advanced PLE techniques is an effective probe of the higher-energy states that are typically inaccessible in standard PL measurements.

Excitation Spectrum of the Exciton Power Law “Fine” structure

In Chapter 3, the superlinear power-law scaling of the exciton PL is used to show that excitons form from a photogenerated electron-hole gas. In Chapter 3, the excitation spectrum of the power law shows evidence of a “fine structure” (c.f. Chapter 3, Figure 4) near the absorption resonances of the high-energy excitons. Near these high energy resonances, the value of the power-law is suppressed back towards a value of approximately unity. This suggests that exciton formation becomes more efficient when photoexciting on an exciton resonance instead of into the continuum states.

By using a tunable narrowband laser, the fine structure of the exciton power law scaling in the Rydberg states of the A and B excitons might be more precisely characterized, potentially providing additional information about how thermalization progresses after high-energy carrier injection. More accurate power-law excitation spectra might also serve as an additional probe of the ultrafast intravalley relaxation that is driven by coulomb exchange interactions⁹.

Twisted Light PLE

Twisted light carries angular momentum in the helical phase fronts of its mode¹⁰ that is predicted to couple to the rotation of the exciton envelope function¹¹⁻¹⁴. Furthermore, the spectroscopic g factor should depend on the winding of the envelope function. Consequently, PLE with twisted light might be able to track these resonances as they shift in an external magnetic field. This study might reveal previously unobserved structures in the energy spectrum of exciton excited states.

Gate Dependence of the Quantum Yield Enhancement effect

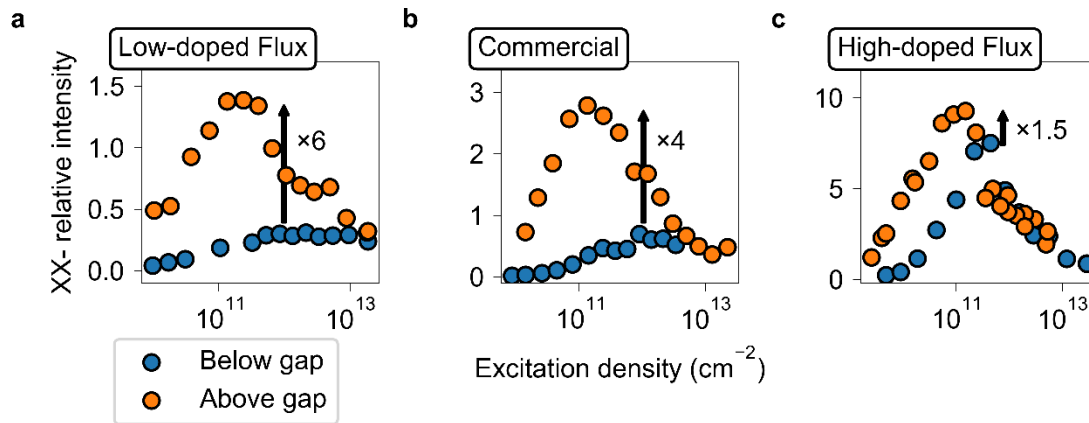


Figure 6.2 – Material dependence of the enhancement of the charged biexciton. Three different samples are shown here: (a) low-doped flux-grown WSe₂, (b) commercially grown (CVT) WSe₂, and (c) more highly doped flux-grown WSe₂. (a-c) the PL intensity of the charged biexciton relative to that of the exciton with below gap excitation (blue) and above gap excitation (orange). The magnitude of the enhancement with above-gap excitation decreases from (a) to (b) to (c).

The role that free carriers play in the enhancement effect reported in Chapter 3 remains an outstanding question. Preliminary experimental evidence compiled by us and shown in Figure 6.2 suggests that the magnitude of the enhancement decreases with increasing carrier density. In these experiments, the enhancement of the charged biexciton is measured in three different samples,

each with a unique level of electron doping and corresponding defect density. As the material quality is decreased, the enhancement of the charged biexciton under high-energy photoexcitation decreases. An electrostatically gated would substantially assist our efforts in fully deconvolving the role of doping versus defects by allowing us to tune the fermi level independently from the defect concentration. Furthermore, a gated device would enable experiments that provide deeper insight into the saturation behavior of the charged biexciton.

Room Temperature Nano-Optical Activation of 2D QEs

Room temperature nano optical characterization of the 2D QEs discovered in Chapters 2 and 3 is perhaps the most exciting direction to take this work. Room temperature single-photon emission has not been demonstrated in a 2D TMD semiconductor. Realizing a protocol to induce

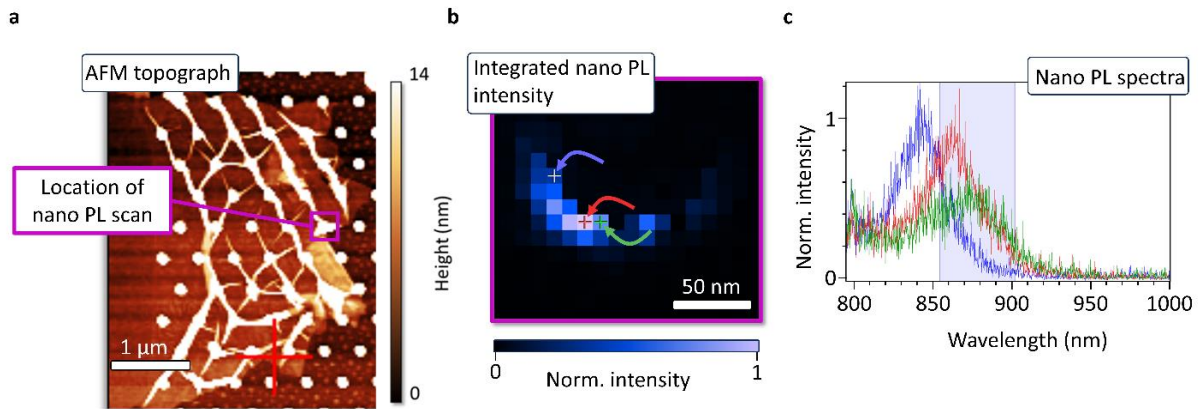


Figure 6.3 – Nano PL of 1L-WSe₂ wrinkle array. (a) An AFM topograph (height map) of the 1L-WSe₂ on Au nano stressors. The location of the nano PL scan is marked by the pink annotation. (b) The integrated nano PL intensity around the apex of an Au cone. (c) Point PL spectra that show localized exciton emission. The spectra in (c) are taken from the locations marked in (b).

QEs in a 2D TMD semiconductor that operates at room temperature would be a significant discovery. Such a protocol would cement 2D materials as a viable platform for scalable quantum photonics that satisfy the requirements of miniaturization and nanoscale positioning.

Nano-optical spectroscopy uses a metallic nano-antenna to probe the surface of a sample¹⁵⁻¹⁷. Commonly, the antenna is a metalized atomic-force microscopy tip. The foundation of the technique is to shine a focused laser onto the apex of the tip to excite a localized surface plasmon and probe the surface of the sample. Consequently, the spatial resolution of nano-optical techniques is dramatically enhanced as compared to far-field techniques. The unique combination of sharp Au nano stressors and the wrinkled 1L-WSe₂ make the samples investigated in Chapters 4 and 5 an ideal platform to conduct nano-optical spectroscopy. Even without the presence of the metalized AFM tip, the Au cones already act as nano-optical antennas. The field enhancement is further intensified in the presence of the nano-optical probe, making the 1L-WSe₂ nano wrinkle array an appealing platform in which to engineer potential room temperature QEs. A nano optical technique is a promising method to brighten the QEs enough to measure their photon statistics at room temperature. Figure 6.3b shows an example hyperspectral nano-PL map taken of 1L-WSe₂ draped over an Au cone in a wrinkle array. In this scan, localized low-energy emission is observed as shown in Figure 6.3c. An outstanding goal is to correlate these localized states that are activated by the nano-optical probe at room temperature to the QEs that are observed in far-field measurements at 4 K to elucidate deep structure-property relationships of 2D QEs and to demonstrate room-temperature single photon emission in a 2D semiconductor. This work is currently underway.

6.3 Final Thoughts

2D semiconductors may prove to be pivotal in accelerating the scalability of some quantum photonic systems. Yet, there are still significant challenges to overcome which require sustained efforts by interdisciplinary teams of researchers. There is more basic science to be done to unravel the formation physics of 2D quantum emitters as well as engineering milestones to hit to achieve efficient and on-demand generation of single photons.

In addition, correlated physics in 2D materials is also an exciting field to explore. Characterizing emergent correlated phenomena with nano-scale resolution is a rapidly developing field with opportunities to utilize cutting-edge characterization techniques to measure novel physical effects.

Finally, through some of the work presented in this thesis, I have gained a deep appreciation for carefully conducted science. I consider myself deeply fortunate to have had the opportunity to learn from and work with an exemplary team of scientists over the past 6 years.

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