Tailoring excitonic light emission of two-dimensional transition metal dichalcogenides semiconductors

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**TAILORING EXCITONIC LIGHT EMISSION OF
TWO-DIMENSIONAL TRANSITION METAL
DICALCOGENIDES SEMICONDUCTORS**

FENG SHUN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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DIMENSIONAL TRANSITION METAL
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FENG SHUN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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This thesis contains material from 1 paper published in the following peer-reviewed journal where I was the first author.

Chapter 3 is published as **Feng, S.**; Cong, C.; Peimyoo, N.; Chen, Y.; Shang, J.; Zou, C.; Cao, B.; Wu, L.; Zhang, J.; Eginligil, M.; Wang, X.; Xiong, Q.; Ananthanarayanan, A.; Chen, P.; Zhang, B.; Yu, T., Tunable excitonic emission of monolayer WS₂ for the optical detection of DNA nucleobases. *Nano Res.* 2018, 11 (3), 1744-1754.

The contributions of the co-authors are as follows:

- Prof. Yu Ting and I conceived the experiment. I conducted the experiments and wrote the drafts of the manuscript. The manuscript was revised together with Dr. Zhang Jing, Prof. Zhang Baile, Prof. Cong Chunxiao and Prof. Yu Ting.
- The sample was prepared by Ms. Wu Lishu, Prof. Cong Chunxiao and Prof. Yu Ting. The optical measurement was helped by Dr. Peimyoo, Namphung, Dr. Chen Yu and Dr. Shang Jingzhi. Device fabrication is helped by Dr. Zou Chenji and Dr. Cao, Bingchen. Dr. Wang Xingzhi and Prof. Xiong Qihua helped on electrical measurement.
- Dr. Ananthanarayanan Arundithi and Prof. Chen Peng provided DNA nucleobase samples, Dr. Eginligil Mustafa provided insights on the nucleobase-2D material interaction.

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Abbreviations

1L	monolayer
2D	two dimensions or two-dimensional
3D	three dimensions or three-dimensional
A	neutral A exciton
A ⁻	(negative) trion
A ⁺	(positive) trion
AA	biexciton
CBM	conduction band minimum
CCD	charge coupled device
COF	covalent-organic framework
CVD	chemical vapor deposition
CVT	chemical vapor transport
CW	continuous wave
DFT	density functional theory
DOF	degree of freedom
DOS	density of state
EBL	electron beam lithography
FET	field effect transistor
FWHM	full width at half-maximum
h-BN	hexagonal boron nitride
HOMO	highest occupied molecular orbital
IPA	isopropanol alcohol
LDH	layered double hydroxide
LHe	liquid helium

LA	longitudinal acoustic
LN ₂	liquid nitrogen
LUMO	lowest occupied molecular orbital
LWD	long working distance
MIBK	methyl isobutyl ketone
MOF	metal-organic framework
PCB	printed circuit board
PDMS	polydimethylsiloxane
PL	photoluminescence
PMMA	poly(methyl methacrylate)
RT	room temperature
SEM	scanning electron microscopy
SOC	spin orbital coupling
TMD	transition metal dichalcogenide
VBM	valance band maximum
vdW	van der Waals

Abstract

The newly emerged two-dimensional transition metal dichalcogenide (2D TMD) semiconductors like MoS₂, MoSe₂, WS₂ and WSe₂ have aroused great interest because of their underlying rich physics and the promising applications in optics, electronics and optoelectronic devices. One of the most interesting properties is the excitonic light emission from direct bandgap in monolayer (1L) semiconductor TMDs, which is easily tailored and can be directly probed by photoluminescence (PL) spectra. In regards of fundamental discoveries, various exciton species in 1L TMDs have been studied including neutral excitons, charged excitons (trion) and biexcitons. However, to further develop exciton physics and device applications, it is of prompt interest to realize artificial manipulation the excitonic emission, which lays foundation of 2D semiconductors-based sensing, computing and light emitting platforms.

In this thesis, we exploited optical, electrical, chemical and micro-/nanofabrication approaches to effectively tailor the excitonic emission of 1L TMDs, in regards of exciton/trion PL spectra weight ratio, valley properties of A excitons and narrow bound exciton emission. We adopted *in situ* PL spectroscopy to probe such evolutions, from which we propose conceivable functionalities based on tunable excitonic light emission of 1L TMDs.

2D TMDs possess a tunable excitonic light emission which is sensitive to external conditions like electric field, strain and chemical doping. Here we reveal the interaction between DNA nucleobases, *e.g.*, adenine, guanine, cytosine and thymine and monolayer WS₂ by investigating the change of the PL emission of the monolayer WS₂ with the coatings of nucleobases solutions. It is found that adenine and guanine exert obvious effects on the PL profile of monolayer WS₂ and cause different PL evolution trends while cytosine and thymine show negligible impact. The p-type doping on WS₂ is clearly evidenced by spectra analysis and electrical measurements.

Beyond previous biosensors which rely on the broad fluorescence signals from label molecules, our findings open a door for label-free optical biosensor directly utilizing the tunable excitonic emission of TMDs and indicate a potential strategy of DNA sequencing detection.

In addition to the PL spectra lineshape, the polarization dependent PL intensity also encodes a lot of information of valley polarized excitons, which correspond to the chirality of emission light. The emerging field of valleytronics has boosted intensive interests in investigating and controlling valley polarized light emission of 1L TMDs. However, so far, the effective control of valley polarization degree in monolayer TMDs semiconductors are mostly achieved at liquid helium cryogenic temperature (4.2 K), with the requirements of high magnetic field and on-resonance laser, which are of high cost and unwelcome for applications. To overcome this obstacle, here we elucidate that by electrostatic and optical doping, even at temperature far above liquid helium cryogenic temperature and under off-resonance laser excitation, a competitive valley polarization degree can be achieved. We observed more than 3-fold monotonical increase of polarization degree of trion emission from 7% to 25% with electrostatic doping. Also, a noticeable enhancement of trion polarization degree is also depicted by increasing excitation laser power through photo-induced electron doping effect. These findings indicate a general doping dependent valley relaxation mechanism, which agrees well with the theory of carrier screening effects on valley relaxation. Our results demonstrate the tunability which corresponds to an effective magnet field of ~ 10 T at 4.2 K. This work not only serves as a strategical reference to future experiments based on valley polarization of monolayer TMDs with various external or native carrier densities, but also provides an alternative approach towards enhanced polarization degree, which denotes an essential step towards practical valleytronic applications.

Along with A exciton emission, defect bound exciton emission also yields great potential as quantum light source. In recent cryogenic measurements, narrow PL peaks at wavelengths of

defect band emission were observed in 1L TMDs, with the capacity of single photon emission, one of mostly promising media of carrying quantum information. However, they are rarely found at random locations, yielding dozens of diverse emitter modes within the broad spectral range, which impedes the precise application. It is of great importance to truly isolate these narrow emissions by the deterministic spatial and spectral control. Here, monolayer WS₂ nanodisks were fabricated by lithography and plasma etching of WS₂ flakes grown by chemical vapor deposition (CVD). The dimension of nanodisks can be effectively tuned by varying the diameter from μm scale to 300 nm, which leads to size dependent PL evolution from broad defect-band emission (line width of ~ 70 nm) to spectrally isolated narrow peaks (line width of $\sim$ sub nm) dominates PL at 4.2 K. The evolution is attributed to strain induced confinement of localized excitons. Importantly, the wavelengths of narrow emissions are highly confined. For same designed disk diameter, more than 80% of peaks are located within 610 to 616 nm, which is better than previously reported native/artificial emitters. Furthermore, the scalable WS₂ nanodisk array is manufactured, demonstrating mass production of isolated emitter-like peaks at identical wavelengths. This approach is also proved effective to confine the defect bound exciton emission in other TMDs like WSe₂. Overall, this work opens new possibilities for future quantum optical communication which can transmit signals at regulated locations and photon energies.

In conclusion, this thesis manifests that the light emission of A exciton, trion and bound exciton in 1L TMDs can be intentionally modified in regards of spectra dominance, PL linewidth and valley polarization. These findings share new insights to low dimensional semiconductor physics as well as the practical prototypes for next generation optical biosensors, valleytronic devices and quantum light sources based on 2D semiconductors.

Publications

1. **Feng, S.**; Cong, C.; Peimyoo, N.; Chen, Y.; Shang, J.; Zou, C.; Cao, B.; Wu, L.; Zhang, J.; Eginligil, M.; Wang, X.; Xiong, Q.; Ananthanarayanan, A.; Chen, P.; Zhang, B.; Yu, T., Tunable excitonic emission of monolayer WS₂ for the optical detection of DNA nucleobases. *Nano Res.* 2018, 11 (3), 1744-1754.
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Chapter 1: Introduction

1.1 Introduction to two-dimensional layered materials beyond graphene

The nanoscale (i.e. 1-100 nm scale at least in one dimension) materials have aroused great attention for their intriguing physical properties and promising applications. One of the beauties of low dimension materials is that they carry novel properties different from their three-dimensional (3D) bulk counterparts, due to the reduced degrees of freedom in certain dimensions [1]. For instance, the 2D layered materials experience the strongest confinement for solids in out-of-plane direction, leading to unusual properties regarding both fundamental physics and practical applications aspects. Since the discovery of graphene in 2004 [2], it has been experimentally demonstrated that it is possible to separate atomically thin layers from the bulk crystals due to the weak van der Waals (vdW) interaction among layers. This carbon monolayer with hexagonal honeycomb lattice structure possess novel symmetry, which leads to unusual electronic structure distinct from graphite. At +K and -K valleys in Brillouin zone, its valance band maximum (VBM) and conduction band minimum (CBM) merge into a single point (Dirac point), resulting in a closed bandgap with a cone-like (Dirac cone) structure. As for the charge carriers near the Fermi level, this electronic band structure drives them to behave like massless Dirac fermions with linear dispersion, leading to ultrahigh carrier mobility up to $10^6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for suspended sample [3]. Despite the early discovery and seemingly simple construction of graphene, abundant studies keep emerging for more than a decade, revealing the new physics and developing new applications like thermal conductors [4], high speed transistors [5], and molecular sensors [6]. As the discoverers, Prof. Andres Geim and Prof. Konstantin Novoselov were consequently awarded the 2010 Nobel Prize in physics, indicating a new era for the Two-dimensional materials-based studies [7].

Figure 1.1 Schematic images of various kinds of 2D materials beyond graphene. Adapted from Ref. [8].

In following years, many family members of graphene have stepped onto the stage as Van der Waals materials with capacities of thinning down to monolayers and exhibit distinctively novel properties [3,8]. As the intrinsic monolayer graphene is a gapless semimetal, great efforts have been devoted in search of layered materials with bandgaps. Group-VI semiconducting TMDs, in form of MX_2 ($\text{M}=\text{Mo}, \text{W}$; $\text{X}=\text{S}, \text{Se}$), stood out to be a proper candidate with bandgap in the visible light to near infrared range. Like graphene, the weak vdW interaction of TMDs guarantees easy exfoliation of monolayers. Surprisingly, the TMDs go through indirect-direct bandgap transition when the thickness is thinned down to monolayers, making them suitable

for optical studies. Due to the quantum confinement in vertical direction and reduced dielectric screening, strong Coulomb interaction dominates the physical properties of the TMDs, which leads to unique optical and electrical properties [9,10]. In addition, the large spin orbital coupling (SOC) and inversion symmetry breaking of 2D TMDs stimulate the highly active research topic of TMD valleytronics [11-13]. Moreover, these 2D semiconductors are reported to demonstrate the single photon emission abilities at cryogenic temperatures, which serve as a potentially ideal light source for future quantum communication and information applications.

This thesis will focus on manipulation of excitonic light emission from monolayer TMD semiconductors. Our studies are mainly conducted on monolayer WS₂, which yield brightest emission in visible wavelengths among 1L TMDs [14]. In **Chapter 1**, basic structure of TMD materials will be introduced, which determines the optical and valley properties of this material. In **Chapter 2**, we review the experimental techniques in sense of sample preparation, device fabrication and characterization methods. **Chapter 3** will depict an optical DNA nucleobase sensing strategy based on evolution of neutral and charged exciton emissions of monolayer WS₂. **Chapter 4** illustrates a detailed investigation that carrier doping is not only able to modify PL spectra components but can tailor the valley polarization as well. **Chapter 5** is an example of deterministically generating narrow bound exciton emission at controlled wavelength by fabricating monolayer TMD nanodisks. **Chapter 6** is conclusion and future perspective regarding optical properties of 1L TMDs.

1.1.1 Crystal structure of 2D TMDs

As mentioned before, in this thesis we focus on Group-VI TMD semiconductors MX₂ (M=Mo, W; X= S, Se). These layered vdW materials can be exfoliated from bulk materials and express long-term stability up to months [15]. This atomically thin layer contains three atoms (sandwich structure (X-M-X)) with unique polytypes based on the stacking order and the coordination of the transition metal atoms. The crystal structure types are classified in three

types with different symmetry properties: 1T, 2H and 3R as shown in **Fig. 1.2**. As for 1T phase which is generally semi-metallic, the crystal exhibits tetragonal symmetry and belongs to D_{3d} point group, the repeat unit is one layer (**Fig. 1.2** (a)). Note that 1H and 1T denote different phase of monolayer TMDs. For the semiconducting phase 1H, 2H and 3R are corresponding to different stacking order of 1H phase. In specific, 3R phase denotes the rhombohedral symmetry and corresponds to D_{6h} point group, with a non-centrosymmetric structure even in bulk form shown in (**Fig. 1.2** (c)). This phase contains three layers as periodic unit. In this thesis we focus on the most stable 2H phase semiconducting TMDs with trigonal prismatic coordination of metal atom, yielding hexagonal symmetry which is classified as D_{3h} point group. Based on this lattice and elements configuration, two distinct properties which are absent in graphene emerges. They are inversion symmetry breaking and spin-orbit coupling, providing a playground for the booming field of TMD valleytronics [16]. The different polytypes lead to various application like catalyst (1T) [17], light emitting (2H) [18] and electronic devices (2H) [19]. The heterostructures/homojunctions of TMDs in different phases are also realized towards enhanced properties, like 2H/1T heterostructure with atomic metal-semiconductor junction [20].

Figure 1.2 Schematics images of the three structural polytypes: (a) 2H (hexagonal symmetry, two layers per repeat unit, trigonal prismatic coordination). (b) 3R (rhombohedral symmetry, three layers per repeat unit, trigonal prismatic coordination). (c) 1T (tetragonal symmetry, one layer per repeat unit, octahedral coordination). Adapted from Ref. [19].

1.1.2 Electronic band structure of 2D TMDs

For semiconducting TMDs, one of the most distinguishable features from graphene is that, the monolayer TMDs possess a nonzero direct bandgap in visible to near infrared range, due to the indirect-direct bandgap transition from bulk to monolayer. Such transition is general for MX_2 semiconductors. In this section we demonstrate the electronic band structure of 2D TMDs with sizable bandgap and strong SOC.

The calculated band structure of MoS_2 is used here as an example [21], for bulk TMDs, the bandgap is indirect from the Γ -point at valence band to the K-point at conduction band in the Brillouin zone. As shown in **Fig. 1.3**, when the layer number is thinning down from 4 layers to monolayer, the energy gap of indirect transition is enlarged while the energy of direct transition within K point is unaffected with reduced layer numbers. Then the energetically favored

transition gradually shifts towards the direct bandgap transition. This evolution in the band structure is attributed to quantum confinement and the consequent modulation in hybridization between p_z orbitals on S atoms and d orbitals on Mo atoms. In specific conduction band minimum at the K-point is relatively immune of the interlayer coupling effect. In sharp contrast, the valence band maximum at Γ -point with p_z orbitals contribution is strongly sensitive to interlayer coupling, which gives rise to the layer dependent band structure evolution. This indirect-direct bandgap transition is further experimentally probed by PL and absorption measurements [9,21]. This finding makes monolayer TMD ideal for optical spectroscopic studies.

Figure 1.3 Band structure evolution of MoS₂ from the bulk form to monolayer. Adapted from Ref. [21].

Then we review the origin of strong SOC, which is another distinctive feature of TMDs compared to graphene. As for the major orbital components at the $+K/-K$ valleys, the conduction band mainly contain d_{z^2} orbital of the transition metal atom, and the valence band

mainly comes from the $x^2 - y^2$ and xy orbitals, calculated by Density functional theory (DFT) [16]. For the main contribution to strong SOC, it is mainly from the d orbitals of metal atom, resulting in spin splitting in scale of hundreds (tens) of meV in the valence (conduction) band [22]. Such strong SOC combined with inversion symmetry breaking leads to unique spin-valley configuration at +K /-K valleys in monolayer TMDs, as shown in **Fig. 1.4**.

Figure 1.4 (a) crystal structure of 2H phase monolayer TMDs. Black and yellow dots denote transition metal atoms the chalcogen atoms respectively. (b) Electronic band structure for TMD monolayers calculated by DFT. E_g denotes the direct bandgap at the K point and the large SOC splitting in the valence band is labeled. Schematic images spin-valley configuration for conduction band and valence band at valleys in monolayer (c) MoX_2 and (d) WX_2 . The optical selection rule for bright exciton transition (spin allowed) is also depicted. Cited from Refs. [23, 24].

As shown in the **Fig. 1.4** (c) and (d), the +K and -K valleys can be selected pumped by circularly polarized light. This band configuration sets the cornerstone for the anomalous high

absorption/emission with valley degree of freedom (DOF), which offers us chances to probe and manipulate these energy states directly in optical spectroscopic experiments [9,10], as discussed in following parts.

1.2 Excitonic emission of 2D materials

1.2.1 The concept of excitons

An electron and a hole are generated in the conduction band and the valence band when a photon is absorbed and induce an inter-band transition in a semiconductor. These photon-generated carriers can attract each other via the electrostatic Coulomb interaction among them, which leads to behaviors distinctively different from free carriers. Under strong spatial confinement as well as reduced dielectric screening, a bound electron-hole pair can be formed. It is an electrically neutral quasiparticle and we call it an exciton. Such electron-hole pair formation further accelerates the optical transition rate.

Figure 1.5 Schematic diagram of 2 kinds of excitons: (a) a free exciton, and (b) a tightly bound exciton. The black dots are atoms. Cited from Ref. [25].

For a conventional free exciton, considering the simplest picture, we may take it as a hydrogenic system like a positronium atom where the electron and hole are rotating in a stable

orbit around each other. Naturally the type of excitons can be differed by the radius of orbit, as free excitons with relatively large radius and tightly bound excitons which are localized in a smaller spatial area near the atom (**Fig. 1.5**). This radius is called Bohr radius which indicates the most possible distribution of the exciton wavefunction. Tightly bound excitons are much less mobile than free excitons, and they have to move through the crystal by hopping from one atom site to another.

Based on the Bohr radius, these two types of excitons are categorized as Wannier or Frenkel type for loosely or tightly bound excitons, respectively. Generally, the Wannier excitons possess the wavefunction across multiple unit cells, which indicates the Bloch band structure of the crystal, and effective mass model is suitable to understand their behaviors. In contrast Frenkel excitons are extremely localized with Bohr radius smaller than lattice constant, thus they cannot be explained by Bloch band theory. In general, in semiconductors most excitons are Wannier excitons, while Frenkel excitons are dominating in insulators and organic crystals. For monolayer TMDs, the exciton type is Wannier excitons, which reflects the electronic band structure of the crystal discussed in previous section.

The binding energy is another benchmark that reflects the type and formation rate of such quasiparticle. It is generally defined as the energy required to break the electron-hole pair into free carriers. For conventional Rydberg type of excitons, the form of binding energy is:

$$E_n = -\frac{\mu}{m_0} \frac{1}{\varepsilon^2} \frac{R_H}{n^2} = -\frac{R_x}{n^2} \quad (1-1)$$

where R_H is the Rydberg energy of the hydrogen atom (13.6 eV), μ is the effective mass of electron-hole pair, m_0 is the mass of electron, ε is the dielectric constant. The quantity

$R_x = (\mu / m_0 e^2) R_H$ introduced here is the exciton Rydberg energy.

As for the Bohr radius,

$$r_n = \frac{m_0}{\mu} \varepsilon_r n^2 a_H = n^2 a_X \quad (1-2)$$

where a_H is the Bohr radius of the hydrogen atom ($5.29 \times 10^{-11} \text{m}$) and $a_X = (m_0 \varepsilon_r / \mu) a_H$ is the exciton Bohr radius. n indicates the atomic state similar in hydrogen atom, e.g. $n = 1$, as the ground state, has the largest binding energy and smallest radius. Like hydrogen atom, higher excited states 2s, 2p, etc. also exist in excitons.

The stability of exciton is indicated by its binding energy versus phonon energy KT . So, for traditional semiconductors with several meV exciton binding energy, it takes low temperature to effectively probe the excitonic absorption/emission. As an example, the formation and population of excitons significantly affect the optical properties of GaAs, seen in **Fig. 1.6**.

Figure 1.6 Absorption spectrum of GaAs under different temperature: The dashed line is a fitting of non-excitonic direct bandgap transition-based spectrum. Adapted from Ref. [25].

The sharp peak in the absorption peaks are attributed to the excitonic transition rather than the direct bandgap e-h recombination. The existence of quasiparticle gives rise to an unusual sharp peak related to exciton energy, in form of:

$$E_n = E_g - \frac{R_x}{n^2} \quad (1-3)$$

E_g corresponds to the direct bandgap of the material. It can be told from **Eq. (1-3)** that the formation of exciton compensates the required energy for transition and yield a higher transition rate compare to direct recombination at the specific value of energy.

1.2.2 Excitons in TMDs

As illustrated before, the reason why it is essential to study 2D TMDs and their analog lies inside the difference between 2D and bulk systems. This vertical quantum confinement of 2D TMDs is orders stronger than 3D GaAs based quantum wells due to the considerably reduced dielectric screening of Coulomb interactions in the true 2D system [7]. This directly leads to the giant exciton binding energy with hundreds of meV, which makes excitons in monolayer TMDs stable even at room temperature [26]. The strong excitonic effect in monolayer TMD combined with direct bandgap brings up anomalously strong PL compared to multilayer counterparts (**Fig. 1.7**), opening a series of optical studies based on monolayer TMDs.

Figure 1.7 PL spectra for mono- and bilayer MoS₂ samples in the photon energy range from

1.3 to 2.2 eV. Inset: PL quantum yield of thin layers for $N = 1-6$. Cited from Ref. [9].

The typical 2D TMDs like MoS₂ or WS₂ possess the binding energy in scale of several hundred meV, in enormous contrast of binding energy of traditional III-V semiconductors like GaAs with value of several meV [27]. Researchers have developed different approaches to experimentally probe the large binding energy of 2D materials like temperature dependent PL [14], two photon excitation spectra [28], reflectance contrast spectrum [26], with a value of 300-500 meV for WS₂. Moreover, it has been discovered that the usual hydrogen Rydberg model described in 1.2.1 no longer stands in 2D system. This unprecedented deviation is originated from the nonlocal reduced dielectric environment that affect Coulomb interaction inside the e-h quasiparticle (**Fig. 1.8**).

Figure 1.8 Schematic images presenting (a) the different confine environment of 2D and 3D

excitons, (b) large binding energy of 2D platform, (c) nonuniform dielectric screening resulting in non-Rydberg atomic states. Cited from Ref. [26].

Another interesting topic is the many-body excitonic states of 2D TMDs, engendering additional kinds of hydrogen-like quasiparticles, including negatively/positively charged excitons (trions) and biexcitons in analogs of H^- , H^+ , and H_2 . Among them trion is firstly discovered, which consist an e-h pair with an additional electron or hole. Generally, with excessive electrons (holes) inside the 2D semiconductor, negative (positive) trion can be formed. One of straightforward ways to probe the trion state is PL characterization, just like for excitons (**Fig. 1.9**).

Figure 1.9 PL spectra of 1L WS₂ at various temperatures. Trion (X^-) and exciton (X) peaks are labeled. (b) PL peak positions at various temperatures. The solid lines correspond to the fitting of the experimental data based on the Varshni equation. Adapted from Ref. [29].

The interplay of spectral weight between exciton and trion mirrors the electron or hole concentration inside the materials, described by the semi-classic Boltzmann distribution [30] from which we can derive the carrier distribution using the relative intensity of two excitonic

states.

With the aggressive carrier injection by electrical/optical gating, excitonic fine structure like biexciton (AA) can also be generated and observed in PL measurements. This quasiparticle consists two pairs of electrons and holes, resulting in different behaviours compared to A excitons. Experimentally, as shown in a **Fig. 1.10**, new PL peak at lower energy side of A exciton will emerge, with increasing charge carrier density via electrostatic doping and/or strong photoexcitation, yielding a superlinear intensity-power relationship [31,32].

Figure 1.10 (a) PL spectra of 1L WSe₂ at various pumping fluences. Trion (X) and exciton (X) peaks are labeled. The emerging biexciton peak is marked in red. (b) Logarithmic plot of the intensity of biexciton as a function of the exciton emission intensity. Adapted from Ref. [31].

At cryogenic temperature, the PL spectra of monolayer WS₂ and WSe₂ show distinctly different character compared room temperature. In addition to exciton and trion emission which are well resolved, new components at lower energy emerges occasionally, with much narrower linewidths than A exciton peaks. They are assigned as localized exciton emission. These sharp emissions are possibly attributed to atomic defects induced trapping potential [32], with possibilities of single photon emissions shown in **Fig. 1.11** [33,34]. **Chapter 5** proposes a

general strategy to engender these narrow emissions and regulate them at close wavelengths by fabricating 2D semiconductor nanodisks.

Figure 1.11 (a) PL spectrum of WSe₂ localized emitters with high resolution spectra of single photon emission and A exciton. (b) Second-order correlation measurement of the PL from the corresponding emitter. The red line is a fit to the data, to extract correlation coefficient $g^2(0) = 0.14 \pm 0.04$. Adapted from Ref. [33].

In addition to these bright excitons, dark excitons are also defined based on the spin orientation of the carriers at conduction band and valence band in the exciton transition. Unlike the bright exciton involving electron and hole of antiparallel spins, for a dark exciton the spins of photoexcited electron and hole are parallel, which forbids the optical transition due to spin momentum conservation. Though, these dark states can be brightened by in-plane magnetic field which breaks the requirement for antiparallel spins [35]. In **Chapter 6**, a future work of brightening dark exciton by exciton-molecule coupling is suggested.

Here the schematic image of different bright exciton transition in TMDs is concluded, with different emission energy due to the various bound states regarding to A exciton and intrinsic bandgaps, these excitonic emission peaks can be separately identified in PL spectra (**Fig. 1.12**). In this thesis we intentionally manifest the spectra weight ratio between trion and exciton as well as circularly polarized PL intensity (i.e. valley polarization) of trion, then depict the deterministic generation of narrow localized exciton with precise spatial and spectral

positioning, towards making better use of the excitonic emission in sensing, computing and optical communication areas.

Figure 1.12 Schematic image of biexciton (E_{BX}), exciton (E_X), trion (E_T) and defect bound exciton (E_{DX}) transitions. While E_B and E_g denote exciton binding energy and bandgap, respectively.

1.2.3 Physically and chemically tailoring excitonic emission in TMDs

As these excitonic transitions in TMDs can be modulated by external conditions, including strain effects [31], chemical/electrical/photo doping [32,33] and temperature effect [14], combined with in-situ methods like gate/temperature/strain dependent PL measurements, both the changes in bandgap and excitonic states can be monitored through the luminescence behaviours. Then it is essential to study the extrinsic properties of 2D materials, as demonstrated in following chapters.

As the excitonic states in 2D semiconductors are highly linked to the carrier concentration, an evolution between the spectral dominance of exciton and trion can be induced by the charge transfer process. One of the methods is gate doping by fabricating transistor device and applying positive (negative) gate voltage, to inject electrons (holes) into the material.

In the gate dependent PL spectra of MoS₂ as the gate voltage increases, a spectral weight redistribution of the exciton and trion emission is generated, where the A exciton is transformed into trion by carrier doping (**Fig. 1.13**). The optical behaviour also contributed to calculate the trion binding energy which describes how much energy it requires to free an additional electron or hole in trion. The energy splitting between the exciton and trion is supposed to have linear relationship with Fermi energy which is proportional to gate voltage. The corresponding relationship can be written as:

$$\omega_A - \omega_{A^-} = E_b + E_F \quad (1-4)$$

where ω_A , ω_{A^-} are emission energy of exciton and trion, E_F is fermi energy, with simple linear fitting the value of trion binding energy E_b is obtained as the intercept (18 meV). The determination of trion binding energy proceeds the fundamental understanding in many-body physics of 2D semiconductors.

Figure 1.13 Electrostatic doping dependent PL spectra of a monolayer MoS₂ under room temperature. (a) PL spectra at different gate voltages. Both the neutral exciton (A) and trion (A⁻) features are assigned. (b) The difference in the exciton and trion energies (i.e. dissociation energy), $\omega_A - \omega_{A^-}$, as a function of Fermi energy E_F . The red line, a linear fit to the E_F dependence, has a slope of 1.2 and an intercept of 18 meV. The latter determines the trion

binding energy. Cited from Ref. [36].

The similar trend can be seen in WSe₂ gated PL work. Compared to natively n-typed doped WS₂, WSe₂ exhibit bipolar behaviour in gated PL measurements, where the positive trion and excitonic fine structures are also detected [37].

Figure 1.14 Excitation power dependent PL spectra of monolayer WS₂ at 4.2 K. (a) PL spectra at various excitation with multiple peak fitting. The exciton species are labeled. (b) PL intensity mapping as a function of excitation power and photon energy powers. Adapted from Ref. [32].

The carrier injection can also be achieved by intensive light excitation, which not only creates electron-hole pairs, but dynamically ionizes the carriers trapped on the donor impurities levels towards conduction band as well [38]. Like the electrostatic gating, this method could promote the emergence of trion even biexciton emission and greatly tailor the PL line shape (**Fig. 1.14**).

Besides the physical tuning, chemical approach to modulate carrier concentration in 2D materials has been developed, which also tunes the PL spectra features. By the physisorption of different kinds of molecules like O₂, H₂O, organic molecules, chemical doping is able to manipulate the excitonic states as well. Compared to electrical doping, the surface molecular accumulation, behaving as a source for introducing carriers, provides much broader tunability of charge concentration and excitonic in some instances [39]. Moreover, chemical doping is free of device fabrication process thus without the risk of contact contaminant or dielectric breakdown. The modulation of quasi particle via chemical route makes possible for multiple

applications, like the sensing of specific molecules or to investigate the environmental effect (i.e. air, moisture, organic solvent) on the 2D samples [40]. Furthermore, as the excitons and trions have different radiative recombination rate, the p-type doping can be useful for the emission enhancement [41].

To probe the chemical doping induced excitonic shift, PL measurement is also the most direct approach, providing a sharp contrast before and after doping, as shown in **Fig. 1.15**.

Figure 1.15 Chemical doping tunable photoluminescence monolayer (a) MoS_2 and (b) WS_2 . Clear excitonic features (A and A^-) and their redistribution are observed. Cited from Ref. [42,43].

The evolution is very easy to notice after the Lorentz peak fitting, after p-type doping the trion component is suppressed while neutral excitons emerges, indicating successful electron transfer from TMD to molecule dopants. In addition, the doping dependent electrical transport provides another evidence of p-type doping [33]. **Chapter 3** is dedicated to exploring the possibilities of optical biosensing and DNA sequencing function based on chemical doping tunable PL emission of monolayer WS_2 .

1.2.4 Valley polarized excitons in TMDs

For crystalline materials with multi-valley structure in Brillouin zone, the term “valley index” is an additional degree of freedom for carriers, which is robust against low energy phonons due to the large valley separation in k-space. To utilize this valley index as an information carrier, the essential step is to achieve a scenario in which the carriers in each valley respond differently to external optical pumping [12]. This process indicates a valley-dependent correlation between valley polarized carriers and circular polarized light excitations, which is in analogy to the spin-dependent optical process in III-V semiconductors like GaAs [25].

As discussed before, the novel SOC combined with inversion symmetry breaking in 1L TMDs give rise to contrasting circular dichroism in +K/-K valleys, which lays the foundation of contrasting optical selection rules at the high symmetry points of the Brillouin zone. It has been proposed that the manipulation of the valley index can be realized through electric, magnetic and optical means [13,44]. Experimentally, optical pumping induced valley polarization in 1L TMDs has been demonstrated beautifully [11, 44], however it requires on-resonance laser excitation and cryogenic temperature to obtain a sizable valley index (i.e. polarization degree), as shown in **Fig. 1.16**. In **Chapter 4** we focus on achieving a competitive valley polarization even at higher temperature and off-resonance excitation.

Figure 1.16 (a) Polarization resolved luminescence spectra of 1L MoS₂ at 1.96 eV excitation and 10 K with the polarization degrees labelled. (b) Circular polarization as a function of temperature. Adapted from Ref. [44]

Chapter 2: Experimental techniques

In this chapter, we introduce the experimental techniques used in this thesis, in regards of sample/device fabrication and optical/electrical characterization. The first part is mainly about the mechanical exfoliation and CVD growth method to obtain monolayer TMD samples. The second part is the main facilities to study the physical properties of monolayer group-VI TMDs, including Raman spectroscopy, PL spectroscopy, electrical transport and cryostat-based low temperature PL measurements.

2.1 Sample preparation

2.1.1 Mechanical exfoliation of 2D TMDs

As developed by professor Andre Geim's team in 2004, monolayer graphene can be exfoliated via mechanical exfoliation of the bulk graphite, known as scotch tape method [1]. The nature of weak van der Waals interaction among stacking graphene layers is similar as in bulk TMDs which ensures such tape exfoliation technique works for TMDs as well. To obtain exfoliated monolayers, first we place the bulk crystal grown by chemical vapor transport (CVT) on a piece of scotch tape/blue tape, which leave some small thick flakes on the tape due to the adhesive force. This piece of tape, serving as source of bulk crystal, is called parent tape. After the initial preparation of parent tape, use another end of clean scotch tape to cover the parent tape and gently press the overlapping part, then peel it off to achieve further thinning of the crystals. This step is repeated several times until the thickness and uniformity of peeled crystals are ready for exfoliation, which can be identified by the "transparency" of crystals on clean tape. Note that the pressing force should be limited, otherwise the thick crystals may break into small pieces which limit the size and yield of monolayers in final products. After the tape with appropriate thickness of TMD crystal is obtained, it is pressed softly onto a precleaned substrate, the air bubbles are squeezed out of the tape to make sure the close contact between tape and substrate, so that the vdW force between the substrate and the crystal would be strong enough

to separate thin layers or monolayers from the bulk form. Note that in some cases polydimethylsiloxane (PDMS) is used as an intermediate medium to exfoliate large monolayers.

Figure 2.1 Exfoliated monolayer WSe_2 . (a) Optical image and (b) the corresponding fluorescence image of exfoliated monolayer WSe_2 .

In this thesis we use Si coated with ~ 300 nm SiO_2 as substrates for exfoliated samples. The interference at the SiO_2 surface provides good optical contrast which can help us roughly identify layer number and locate the desired flakes under conventional microscopes.

There are two main benefits of mechanical exfoliation method. First is that it is most facile method to obtain layered TMD crystals without requirement for complicated growth or liquid exfoliation. The second advantage is, thanks to the inherited high qualities from bulk crystals, the exfoliated TMD monolayers generally display higher qualities in sense of uniformity, PL brightness and defect densities, which is suitable to conduct fundamental research and reveal new physics in this class of material. However, solely from mechanical exfoliation, the monolayers can only be scarcely found with limited sizes, ranging from few to tens of μm (**Fig. 2.1**). This limits the further scalable fabrication and on-chip integration of TMDs.

2.1.2 Chemical vapor deposition growth of 2D TMDs

To overcome the size limitation of exfoliated monolayers towards large even wafer-scale monolayer TMDs, CVD method is developed [14,45-47]. The major principle to grow TMDs is the direct sulfurization/selenization of transition metal oxides on the SiO_2/Si substrate.

Figure 2.2 Schematic of the CVD system for the growth of MS_2 ($M=\text{Mo}, \text{W}$).

As depicted in **Fig. 2.2**, here we designed a customized method to direct sulfurize the WO_3 on SiO_2/Si substrate using atmospheric pressure chemical vapor deposition method. The oxide source can be either powders or spin-coated film [48], the latter approach guarantees precise oxide concentration control and leads to large monolayer flakes with high coverage. Note that here the sulfur is heated separately at constant temperature to ensure the stable supply of sulfur source [14]. The optimized growth recipe for our system is around 750 to 800 °C with 300 sccm Ar gas flow. This configuration is also compatible with sapphire substrates, with slightly higher growth temperature. The sample grown on sapphire are generally better in sense of emission uniformity and flake coverage, the as-grown flakes/films on sapphire are also easily transferred [49] to other substrates like glass or mica. In some instances, the NaCl power is mixed with WO_3 as catalyst to promote the growth of large-area flakes [47,50].

Figure 2.3 CVD grown monolayer WS_2 . (a) Optical image of CVD grown monolayer WS_2 on SiO_2/Si substrate. (b) Fluorescence image monolayer WSe_2 . (c) Optical image of CVD grown monolayer WS_2 on sapphire substrate. (d) Optical image of CVD grown monolayer WS_2 transferred from sapphire to glass substrate. White lines denote the edge of monolayers, within the marked lines are monolayer regions with slightly different contrast.

Fig. 2.3 shows our products of CVD grown monolayer WS_2 . It is clearly depicted that the sample size is exceeding mm scale on both SiO_2 and sapphire substrates, which is two orders larger than exfoliated monolayers. Such scalable production of monolayer samples opens up possibility for large-scale fabrication of nanopattern arrays, as discussed in following chapters. The fluorescence image suggests bright emission intensity which is suitable for many applications like light emitting diodes, gain medium for lasing and optical sensing.

2.1.3 Fabricating TMD nanopatterns

As discussed before, 2D materials are natural quantum well with ultimate confinement in vertical direction (0.7 nm thickness for monolayer WS₂). It is of great interest to design lateral confinement as well, which could lead to novel behaviors of phonons [51,52], excitons [53] and electrons [54,55]. As we have obtained large-area monolayer samples, it is applicable to etch them into nanopatterns with determined sizes and shapes by electron beam lithography (EBL) followed with plasma etching. The details of fabrication are discussed below.

First, we spin coat a thin layer of electronic photoresist, Poly(methyl Methacrylate) (PMMA) on as-prepared 2D materials on Si/SiO₂ wafer, followed by baking on a hot plate at 175 °C for 1 min, which hardening the PMMA and enhances the EBL resolution. After locating the desired sample position under optical microscope, EBL is performed with Zeiss Auriga system, using nanopatterning software by which we can designed the lithography patterns. The shape, size and arrangement of nanopatterns can be precisely programmed. We can also easily design the nanopattern arrays on large flakes, which consist units of identical or continuously varied sizes. The e-beam resolution is down to 500 nm with 20 KV electron high tension voltage. After the EBL, the wafer is immersed in a mixed solution of isopropanol alcohol (IPA) and methyl isobutyl ketone (MIBK) for developing process, which exposes the patterned area. Subsequently, the substrate is placed in plasma chamber for Ar/O₂ plasma treatment. Before the etching the chamber is pumped to high vacuum, then the radio-frequency voltage is applied to the Ar/O₂ gas, and high-energy plasma is formed inside the chamber for etching treatment, which eliminates the exposed monolayers. Generally, the treatment time is 100-130 s to completely etch the unwanted monolayers. After etching the substrate is immersed in acetone for several hours to lift off the PMMA and the 1L nanopatterns are obtained. The process is schematically shown in **Fig. 2.4**.

Figure 2.4 Flow chart of fabricating 2D TMD nanopatterns based on as-prepared TMD samples.

The size and shape of nanopatterns can be conveniently varied across same monolayer flake, to reveal new physical properties with reduced dimension (**Fig. 2.5**). The scalable nanopattern array can be fabricated as well, which is compatible to silicon process and on-chip integration, towards deterministic production of high-quality gain medium for next-generation nanophotonic applications.

Figure 2.5 Fluorescence images of (a) monolayer WS_2 microdisks and (b) nanoribbons with designed patterns on SiO_2/Si substrate.

2.1.4 Device Fabrication

To investigate the electrical properties of 2D TMDs and tune the carrier density inside sample, back-gated field effect transistors (FETs) are fabricated based on EBL. **Fig. 2.6** illustrate the schematic flow chart for device fabrication process.

Figure 2.6 Schematic image of device fabrication process based on 2D TMDs.

The EBL process is similar to nanopatterning part discussed above, except that electrode patterns are much larger than nanopatterns especially for the large Au pad ($\sim 300\text{ }\mu\text{m}$), which require higher electron-beam dose. After development process, the patterned area for electrodes are exposed. Subsequently, the wafer is deposited with metal contacts 5 nm/80 nm of Cr/Au, by thermal evaporation. After taken out, the wafer is immersed in acetone for several hours to lift off the PMMA and undesired metal film. Optical images of device fabrication process are shown in **Figs. 2.7** (a)-(c). Note that this fabrication process is general for other 2D materials and heterostructures with limited thickness (**Fig. 2.7** (d)).

Figure 2.7 Optical image of CVD WS_2 (a) as grown, (b) after EBL patterning, (c) after fabrication. (d) MoS_2/WS_2 heterostructure with electrodes for gated PL measurements. Inset is the fluorescence image of heterostructure with $15\text{ }\mu\text{m}$ scale bar.

2.2 Optical characterization

2.2.1 Photoluminescence Spectroscopy

As discussed in chapter 1, the light emission of TMD semiconductors is strongly correlated to the electronic band structures, here we depict how the light excitation induces interband transition and results in strong light emission, which reflects the band structures and strong Coulomb interaction among photo-excited carriers.

The photoexcitation injects electrons in conduction band and hole in valence band initially, for Stokes PL this requires incident light with photon energy higher than the bandgap. However, these excited electrons (holes) lose the energy very fast by phonon emission and relax towards the CBM (VBM), schematically shown in **Fig. 2.8** (a). Each relaxation step corresponds to a phonon emission which meets the energy and momentum conservation laws. Note that relaxation process is orders faster than radiative recombination of electrons and holes at band edge. The densities of states of electrons and holes accumulated near band edge can be quantitatively estimated by Boltzmann distribution as well (**Fig. 2.8** (b)). Importantly, the sizable exciton binding energy and SOC in monolayer TMDs also modifies the emission energy greatly, as discussed before in **Chapter 1**.

Figure 2.8 Schematic image of (a) carrier relaxation and recombination during photoluminescence. The corresponding phonon emissions are labeled. (b) Level occupancies for photo excited carriers. The shading denotes the distribution function estimated by Boltzmann statistics. Cited from Ref. [25].

The PL features of 2D TMDs has been widely discussed in previous chapters, here we focused on experimental setups of PL measurements, which contribute most of our experimental results in regards of light emission from 2D semiconductors (**chapter 3-5**).

All the PL spectra measured at room temperature (**Chapter 3**) and 80 K (**Chapter 4**) are collected by the WITec Confocal Raman system (alpha 300). The corresponding schematic diagram and beam path are shown in **Fig. 2.9**. The Koehler white light is used to illuminate and focus the sample. The optical images are monitored by the reflected light collected in video camera. The continuous wave (CW) laser beam with wavelength of 532 nm is coupled into the microscope via a single-mode optical fiber and then collimated with an adjustable optics to a parallel beam. Then the beam is directed by the beam splitter to the microscope objective, through which it is focused onto the sample. The laser spot diameter on the sample for 532 nm laser is around 500 nm (1.2 μm) for 100x (50x) objective lens. The collection system in a backscattering configuration, which allows the lens to collect the scattered light for Raman signals. This Raman system can be further modified with quarter wave and linear polarizer insertion and stage replacement. For room temperature measurements the sample is mounted at a XYZ stage precisely adjusted by piezoelectric control, which can move manually to locate the sample under microscope.

We have two major PL configuration for the works in **chapter 3, 4**. First one is for room temperature PL in ambient environment, without polarization resolved features. Second one is for low temperature (80 K) with capacities of capturing lineally/circularly polarized PL. The

sample is sealed in Linkam stage in high vacuum (10^{-3} mbar) and connected to semiconductor characterization system (Keithley 4200) for in-situ electrostatic doping.

2.2.2 Raman spectroscopy

Raman spectroscopy is a well-known spectroscopic observation to probe vibrations and rotations of atoms or molecules based on Raman scattering, which reflects the energy difference of the scattered photons compared to the incident photons during the light-matter interaction. In details, when a crystal is excited with light, in addition to the reflection, transmission and absorption of light, some the incident photons are scattered by the molecules or phonons in the material. The major type of such scatterings is elastic scattering, where the energy is identical for scattered photon as that of incident photon. For instance, Rayleigh scattering is a typical elastic scattering. While a minority of the incident light goes through the inelastic scattering, where the incident photons gain or lose energy. Raman scattering is referred to a common inelastic scattering of the photons. The energy loss in Stokes Raman is consistent with the phonon energy due to energy conservation, and generally corresponds to the Raman shift in Raman spectra. Thus, Raman spectroscopy provides a precise visualization of crystal vibration modes [56]. It can be conducted with same facilities for PL measurements.

Experimentally, in this thesis the Raman spectra and mapping of TMDs are obtained using the same Witec confocal Raman system introduced in **Chapter 2.2.1** with 1800 grooves/mm grating. We conducted room temperature Raman spectra/mapping measurement using this system in **Chapter 3**.

Figure 2.9 Schematic diagram of WITec Confocal Raman system. Adapted from Ref. [57].

2.3 Electrical measurements

In this thesis we focused on two types of electrical measurement based on back-gate transistors. First one is electrical transport measurement. For transport the we measure drain–source current (I_{ds}), while drain source bias voltage (V_{ds}) is fixed at the TMD channel and the back-gate voltage (V_g) is swept from negative to positive. This transport property indicated the electrical response of sample upon carrier injection. The second purpose is in-situ electrical doping, as discussed before. In this measurement we switch off the drain source voltage and fix the V_g for each PL spectra to tailor the carrier densities inside the sample. We connected our device to semiconductor device analyzer either by vacuum probe station (transport measurement, **Chapter 3**) or wire bonding to external printed circuit board (PCB) chip. (gated PL, **Chapter 3,4**). In semiconductor analyzer (Keithley 4200) we are able to set the voltage values for gate and drain-source voltages and measure the drain-source current with applied voltages. An example of gated PL configuration is shown in **Fig. 2.10**, as displayed in the

software panel, the back-gate voltage is set at -5 V and drain-source voltages is switched off. Then the Keithley 4200 could constantly feed the sample with vertical voltage bias.

Figure 2.10 Software panel of Keithley 4200, configuration for gated PL measurements.

2.4 Cryogenic measurements

2.4.1 Linkam stage

The Linkam stage is a small cryostat with convenient connectivity to external semiconductor device analyzers, which can seal the sample in vacuum and cool it down to 80 K. All the gate

dependent and/or polarization resolved PL measurements were conducted with this stage at room temperature (**Chapter 3**) or 80 K (**Chapter 4,5**).

For Low temperature (80 to 300 K) measurements, the XYZ stage is replaced by a Linkam cryostat which can be cooled down to 80 K by liquid nitrogen (LN_2), and the 100x objective lens is changed to a 50x long working distance (LWD) objective accordingly. The configuration of Linkam stage is shown in **Fig. 2.11**, the LN_2 cooling cycle, vacuum pumping, opened window for optical measurements and external connections to semiconductor analyzer and temperature panel are labeled.

Figure 2.11 (a) Schematic diagram and (b) optical image of Linkam stage.

2.4.2 Customized magneto-Raman/PL System

To further cool down the temperature to 4.2 K for optical studies, we adopted the custom designed magneto-Raman system (attocube) for Helium cryogenic temperature measurements, based on a commercial WITec confocal Raman spectroscope. As shown in the sketch map (**Fig 2.12 (a)**), the main body of the magnet system is a liquid helium (LHe) bath, which can provide the crucial stability and remain temperature at 4.2 K for days, in addition the superconducting magnet is installed inside the cryostat which provides high magnetic field from -9 to 9 T in out-of-plane direction with LHe supply. Samples are mounted on the non-magnetic stage, which is made of three-axis piezo positioners. Note that the scanner table enables the

PL/Raman/photocurrent mapping, which is crucial for detailed demonstration of spatial distribution of signals, as shown in **chapter 5**.

As for the optical characterization, we installed an optical head at the top of cryostat (**Fig. 2.12**). The general configuration is similar to previously discussed Raman system. We rely on the white light illumination and reflected signal to the charge coupled device (CCD) to visualize and locate the sample. After focusing, we excite the mounted sample with 532 nm CW laser. The light emission is collected by spectrometer. The polarizers and quarter wave plate along the beam path can be optionally inserted to acquire polarization resolved PL spectra.

Figure 2.12 (a) Schematic of customized magneto-Raman/PL system. (b) The optical head. Adapted from Ref. [58].

Chapter 3: Tunable excitonic emission of monolayer WS₂ by DNA nucleobases

3.1 Introduction and motivation

Two-dimensional transition metal dichalcogenides (2D TMDs) have attracted increasing attention due to their extraordinary optical and electrical properties [19,23,60]. Unlike graphene, monolayer semiconductor TMDs, MX₂ (M = Mo, W; X = S, Se), possess a direct bandgap in the visible to near infrared range which can give rise to an anomalously strong PL emission [9,10]. The 2D confinement results in reduced dielectric screening and enhanced coulomb interactions, which further lead to relatively large binding energies of the electron–hole (e–h) quasiparticle like neutral excitons (A), charged excitons or trions (A[−]/A⁺) and even biexcitons (AA) [32,36]. These excitonic states are strongly correlated to the unique electronic structures of 2D semiconductors and are reflected by sharp and intense peaks in the PL spectra of these 2D semiconductors. Therefore, the energy and related emission states can be manipulated by tuning the electronic structure, such as gate/chemical doping [43,60], applying an external strain [61], and laser stimulation [62] and probed directly by optical and electrical measurements. Among these methods, the modulation of excitonic states via chemical approaches, has become a promising research direction not only due to the efficient improvement of optical properties of 2D semiconductors by the chemical treatment [41,63] but coupling between the chemical compounds and 2D materials indicates chemical sensing ability, arising from their large surface to volume ratios. Many efforts have been devoted to the study of charge-transfer-induced interactions between 2D semiconductor TMDs and its surroundings including environmental molecules like H₂O, O₂ and typical dopants like F4TCNQ [39,42]. To date, the investigation of interaction of biomolecules with 2D semiconductor TMDs is in its infancy, and most of the studies are in theoretical points of view. To date, experimental reports have focused on the fluorescent (FL) or chemiluminescent detection of DNA using liquid-

phase exfoliated nanosheets of 2D semiconducting TMDs for optical sensing [64-67]. Specifically, the optical signals of these platforms originate from the fluorescence label molecules rather than the TMDs. In sharp contrast, the observation of tunable excitonic emissions directly from monolayer TMD samples upon the physisorption of biomolecules is rare, especially for the well-analyzed excitonic emission (A/A^-) features hidden in the spectra [68]. In this work, such changes in the PL spectra of 2D TMDs, which have been underestimated in previous biosensing studies, are monitored and shown to be useful biosensing indices. Compared to liquid-phase TMD samples in solution, solid-phase flakes on Si/SiO₂ wafer substrates are more suitable for developing sensing devices integrated on chips. For such applications, the exploration of the sensing abilities of chemical vapor deposited (CVD) TMDs is an essential step. Meanwhile, the CVD process could be used for mass production of these materials. Studies of the PL detection of biomolecules using CVD 2D semiconductor TMDs are scarce but crucial for the development of biosensing applications.

In recent years, researchers have made considerable efforts to use the 2D materials as platforms for biological fluorescence sensing and imaging studies [69-71]. Among the various sensing targets, the development of a convenient label-free DNA detection platform with low cost has gained explosively increasing interest [72,73]. Recently, several methods for detection of specific DNA strains with TMDs based on Förster resonance energy transfer (FRET) pair were reported [74]. However, these sensing tactics require complicated probe-target labelling process, leaving the area of optical one-step detection undiscovered [64,75]. Furthermore, the main focus of previous studies is on the larger molecules like particular DNA strands, while the detection of basic nucleobases that form the strain is less noticed. Given the genetic information of DNA is hidden inside the sequence of these fundamental bases, compared to the recognition of a certain DNA strain, the detection of single bases can serve as an alternative pathway to potentially decode countless kinds of DNA molecules within one platform, leading

to a possible solution for optical DNA sequencing [76]. In these regards, one step approach of optical detection of nucleobase with 2D materials is worth developing. Note that semiconductor TMD materials stand out to be a proper candidate due to its chemically tunable excitonic proprieties. To achieve such optical sensing applications, investigating the impact of DNA bases on optical properties of semiconductor TMD material would be a valuable start.

Figure 3.1 Characterization of WS₂ flakes. (a) Optical and (b) fluorescence images of CVD grown 1L WS₂ sample on SiO₂/Si substrate. (c) Lorentz-fitted Raman and (d) PL spectra of the WS₂ flakes at room temperature in air.

3.2 Experimental details

3.2.1 Sample preparation

Monolayer WS₂ flakes were chemically grown on a 300-nm SiO₂ layer capped on a highly doped Si wafer using CVD. We followed a method employed in previous studies on WS₂ growth [14,45]. The prepared samples are symmetric and triangular with strong and homogeneous fluorescence emissions, as shown in **Figs. 3.1** (a), (b). For the WS₂ transistor device, the sample was produced by mechanical exfoliation from commercial bulk WS₂ crystals purchased from 2D Semiconductors Inc., also onto highly doped 300 nm SiO₂/Si wafer.

All DNA nucleobases powders were purchased from Sigma-Aldrich (Singapore). The powders were dissolved in conventional organic solvents (ethanol and isopropyl alcohol) and water and sonicated for 30 min to obtain clear solutions with micro- to millimolar concentrations. The as-prepared solutions and solvents for the control experiment were spin coated onto the wafer at 1000 rpm for 60 s to avoid leaving residues because of the liquid–substrate affinity.

3.2.2 Device fabrication and characterization

A 5-nm layer of Cr and an 80-nm layer of Au as source and drain electrodes, respectively, were deposited by thermal evaporation after using a standard electron beam lithography process to pattern the contact electrodes, followed by a lift off process in acetone to obtain well-defined metal electrodes. All electrical transport measurements were conducted under vacuum (10^{-5} mbar) at room temperature using an Agilent Technologies B1500A semiconductor device analyzer.

3.2.3 Optical characterization

The micro-PL and Raman measurements were performed with a WITec Alpha 300 system. We used an excitation laser with a wavelength of 532 nm for the PL and Raman measurements.

The laser power was kept lower than 60 μW to avoid heating effects. The gate-dependent PL measurement was conducted using the same WITec system with the substrate loaded into the Linkam stage and connected with a Keithley 4200-SCS semiconductor characterization system. The configuration remained the same before and after the solution was spin coated.

3.3 Results and discussion

3.3.1 Basic characterization of WS₂ flakes

The CVD samples show symmetric triangular shape with strong and homogeneous fluorescence emissions, as shown in **Fig. 3.1** (a), (b). To further characterize the sample quality, Both PL and Raman spectra are measured with 2.33 eV (532 nm) continuous laser (only A exciton is observed). In **Fig. 3.1** (c), the interpreted Raman features indicate our sample is highly crystallized WS₂ which contains phonon modes of in-plane vibrational $E_{2g}^1(\text{M})$ and $E_{2g}^1(\Gamma)$ mode, the second-order mode of longitudinal acoustic phonon $2\text{LA}(\text{M})$, an out of-plane A_{1g} mode and some combinational modes. A frequency gap of 62 cm^{-1} between $E_{2g}^1(\Gamma)$ and A_{1g} is observed. These signatures agree well with previous Raman studies of monolayer WS₂ [77-80]. **Fig. 3.1** (d) shows PL spectra of the as prepared sample, where the distinct peak with emission energy at 1.96 eV is observed. The peak position agrees well with reported range of A exciton emission of CVD-grown monolayer (1L) WS₂ at room temperature [14,80]. By Raman fingerprints and striking PL emission, we confirm that we confirmed that the monolayer WS₂ was obtained. The PL intensity of as grown CVD WS₂ is intrinsically stronger than MoS₂ [14] even without any further chemical treatment [41,63], making it more suitable for optical applications.

Concerning the shape of the PL spectrum, based on a previous study, it mainly contains peaks originating from two kinds of quasi-particles: neutral and charged excitons. Generally, if there are excessive electrons (holes) inside the sample, negative (positive) charged excitons could be formed [36]. Compared to the A, A^-/A^+ consist of an e-h pair with an additional electron or

hole, resulting in different recombination behaviors and emission energies. Both states can be identified in the PL spectrum by peak fitting and assignment because of their different peak positions and peak widths. Therefore, the PL profile of WS₂ is sensitive to the charge transfer induced by the adsorption of p/n-type dopant molecules.

Figure 3.2 Optical detection of DNA nucleobases. (a) Schematic image of the optical nucleobase sensing platform, and (b)–(e) PL spectra of 1L WS₂ before and after being coated with 1 mM adenine, guanine, thymine, and cytosine solutions, respectively.

Figure 3.3 Control experiments. (a) The PL spectrum before and after the ethanol is spin coated on the WS₂ sample. (b) The decomposed PL spectrum before and after the 1 μ M adenine solution is coated on the WS₂ sample.

3.3.2 Optical response of DNA nucleobases on WS₂

As shown schematically in **Fig. 3.2** (a), the as-grown WS₂ on the SiO₂/Si wafer was spin coated with a DNA nucleobase solution and then exposed to laser light to record the PL spectra before and after the spin coating of the nucleobase solution, which makes it possible to study the effect of the nucleobases on WS₂ systematically. To validate that the optical responses arose from the nucleobases alone rather than solvent (ethanol), we conducted control experiments. The PL spectra (**Fig. 3.3** (a)) recorded before and after the spin coating of pure ethanol on the sample contain identical features, which indicates that any further evolution is from the solute (i.e., nucleobases) rather than the solvent. In addition, this control experiment eliminates the potential interference of moisture doping from the ambient environment [39,43]. The effects of four kinds of nucleobases on WS₂ were probed by PL measurements before and after coating with a 1 mM nucleobase solution, as shown in **Figs. 3.2** (b)–(e). We found that adenine and guanine exhibit quantitatively different splitting effects on the PL profile (**Figs. 3.2** (b), (c)),

while cytosine and thymine (**Figs. 3.2** (d), (e)) have a negligible impact on the PL features of WS₂. The different effects of the nucleobases on the PL features of WS₂ provide a convenient approach and rich possibilities for detecting and distinguishing the four bases.

The evolved PL features in **Figs. 3.2** (b)–(e) can be further decomposed into multiple Lorentz peaks. Based on the fitted curves and referring to the literature [43], the lower energy peak can be identified as a negative trion, A[−] (1.96 eV), whereas the higher energy peak originates from a neutral exciton, A (2.01 eV). In the spectra of WS₂, after coating with A/G bases, the neutral exciton A peak emerges and dominates the PL spectra. A similar evolution is observed in the gate [32,37] and chemically modulated [39,42,43] PL measurements. Based on these reports, this splitting signature is attributed to p-type doping. Because adenine gave rise to a more pronounced emerging neutral exciton peak compared to guanine, it is worth identifying the factors that dictate the magnitude of this optical evolution. Thus, we used adenine as an example to probe this PL splitting effect comprehensively and confirm its physical origin using multiple electrical approaches.

To further understand the adenine-WS₂ coupling effect, concentration-dependent PL measurements were performed and analysed. Several as-prepared samples that exhibit trion-dominated emission were tested after the spin coating of adenine solutions of different concentrations. As shown in **Fig. 3.4** (a), with increasing concentration, the integrated intensities of the A[−] and A components evolve oppositely. Using the same Lorentz fitting analysis discussed before, as the concentration rose from 1 μM to 2 mM, the spectral weight of the A[−] component decreased, while the weight of A component increased. This excitonic evolution caused a continuous transformation of the overall PL features.

Figure 3.4 Further investigation of the effect of adenine on excitonic emission and electron density of WS₂. (a) PL spectra of WS₂ doped under different adenine solution concentrations,

from 1 μM to 2 mM. (b) Integrated intensities of charged and neutral excitons derived from the Lorentz fitted spectra in (a). Inset shows the values of I_{A^-}/I_A and n_e under different solution concentrations with error bars. (c) The calculated electronic band structure of WS_2 and adenine, indicating the electron transfer direction.

The similar trend has been reported in recent chemical doping works [81]. Such quantitative control of many-body states is also intrinsically correlated to the modulating of electron densities of the sample, as interpreted in **Fig. 3.4** (b) and also in band alignment (**Fig. 3.4** (c)). Theoretically, the relationship between the electron density n_e and integrated PL intensity of A^- and A (I_{A^-} and I_A) can be modeled by a simplification from rate equation and mass-action law [36]:

$$n_e = \frac{I_{A^-}}{I_A} \cdot \frac{\gamma_A}{\gamma_{A^-}} \cdot \frac{4m_x m_e}{\pi \hbar^2 m_{x^-}} \cdot K_b T \cdot \exp\left(-\frac{E_b}{K_b T}\right) \quad (3-1)$$

where γ_A and γ_{A^-} are radiative decay rates of A^- and A , m_{x^-} , m_x , m_h and m_e are effective masses of A^- , A , holes and electrons, respectively, where $m_{x^-} = 2m_e + m_h$ and $m_x = m_e + m_h$, $\hbar$ is the Planck's constant, K_b stands for the Boltzmann constant, T is room temperature, E_b is the binding energy of A^- . Then a proportional relationship for the n_e and I_{A^-}/I_A is established after prudent consideration of values of other terms. Specific discussion for the approximation and choices of constant values can be seen in **Chapter 3.3.3**. Based on this linear relationship, using the given type of materials and experimental conditions (E_b , γ , K_b , T ...), the n_e can be obtained from decomposed PL features under different adenine concentration, which yields the I_{A^-}/I_A values. The derived value of n_e monotonically decreased from 8.8×10^{13} to $2.4 \times 10^{13} \text{ cm}^{-2}$ as the solute density increased by 3 orders of magnitude. Previous investigations of the chemical doping of 1L WS_2 have reported similar n_e values [8].

3.3.3 Estimation of electron density via PL spectra of monolayer WS₂

We referred to the mass action law to estimate the electron density in 1L-WS₂ sample. The equation describes the relationship between exciton population N_A/N_{A^-} and electron concentration n_e [82]:

$$\frac{N_A n_e}{N_{A^-}} = \left(\frac{4m_A m_e}{\pi \hbar^2 m_{A^-}} \right) K_b T \exp\left(-\frac{E_b}{K_b T}\right) \quad (3-2)$$

To directly obtain n_e from the as measured spectroscopic data (i.e. integrated intensity I_{A^-} , I_A), following approximately simplified transformation is required

$$\frac{I_{A^-}}{I_A} = \frac{\gamma_{A^-} N_{A^-}}{\gamma_A N_A} \quad (3-3)$$

Combine **Eq. (3-2)** and **Eq. (3-3)** then proportional relationship for the n_e and $\frac{I_{A^-}}{I_A}$ is obtained as shown in the **Eq. (3-1)**:

$$n_e = \frac{I_{A^-}}{I_A} \cdot \frac{\gamma_A}{\gamma_{A^-}} \cdot \frac{4m_A m_e}{\pi \hbar^2 m_{A^-}} \cdot K_b T \cdot \exp\left(-\frac{E_b}{K_b T}\right) = 0.155 \times 10^{14} \cdot \frac{I_{A^-}}{I_A}$$

Here what worth noting is that the approximation we adopted is referred to previous theoretical analysis, in which radiative decay rate γ is regarded as constant under different carrier density for the change of γ is neglectable in our experimental range [36,42]. As for the exact values to determine the proportional factor, recently there is a work reporting the computed values for neutral exciton lifetimes for MoS₂ and WS₂ but the trion lifetime is absent [83]. Cui et. al have applied assumed values of exciton lifetime to perform their fitting based on an exciton population model and also got reasonable result [84]. Therefore, we anticipate the ratio of quasi particles (A and A⁻) decay rate in WS₂ to be in similar scale to the reported experimental values monolayer MoS₂ [85]. $\gamma_A = 0.002 \text{ ps}^{-1}$, $\gamma_{A^-} = 0.02 \text{ ps}^{-1}$, m_e and m_h are $0.44m_0$ and $0.45m_0$ [23], E_b is 38 meV [14] while $K_b T$ equals to 27 meV under room temperature. With the help of these coefficients we can determine the n_e via PL excitonic status of 1L WS₂ under different concentration of adenine solution.

3.3.4 Discussion of base-TMD interaction

This tailoring of the PL feature agrees well with the previous experimental and theoretical reports [86]. Our finding is consistent with those of a previous electrochemical investigation, which reported the electron withdrawing ability of adenine and guanine on TMDs [68]. Regarding theoretical analysis, the potential interaction mechanism between the bases and WS₂ can be understood from a microscopic point of view, considering the anchoring force, stacking configuration, and doping effects. After spin coating the nucleobase solution, the base molecules are physisorbed onto the WS₂ surface. The binding energy and distance were estimated to be around 0.2 eV and 4 Å [86-88], respectively. Based on calculations [86,88], guanine and adenine generally have larger binding energies than cytosine and thymine, which indicate stronger interactions and agree with our PL responses. The possible geometries of the nucleobases with respect to the WS₂ basal plane have also been suggested, from parallel [88] to tilted by up to 40° [89]. The large tilting angles can be possibly attributed to concentration-induced stacking effects [43] and the presence of defect sites [60,90] or solvent molecules [87] on the sample surfaces, which could strongly interact with the base molecules. Subsequently, an interfacial dipole between the base and WS₂ is generated, enabling the charge transfer process, which was calculated to be 0.01e per nucleobase molecule on a 5 × 5 WS₂ unit cell [86]. This doping effect was equivalently predicted by the pronounced modification of the work function/Fermi level and density of states (DOS) of WS₂ [91]. The depletion of electrons is caused by charge transfer between 1L WS₂ and adenine, as schematically shown in **Fig. 3.4**. Considering the band alignment, **Fig. 3.4** (c) shows the computed minimum of the conduction band (−3.84 eV) and the maximum of the valence band (−5.82 eV) of 1L WS₂, as well as the highest occupied molecular orbital/lowest occupied molecular orbital (HOMO/LUMO) energies of adenine [91-93]. The as-grown sample is intrinsically n-doped, as reflected by the trion dominated PL features, which leaves the Fermi level of 1L WS₂ above the bottom of the

conduction band. This band offset results in a charge transfer process from WS₂ to adenine, which neutralizes the WS₂ sample and diminishes trion formation. As the concentration of adenine coated on WS₂ increased, more electrons were extracted from the as-grown n-doped sample, resulting in the further excitonic evolution of the PL feature.

Our findings indicate that, upon the physisorption of adenine, the electron density of 1L WS₂ is strongly modulated. In addition, the spectral weight transformation from A⁻ to A indicates the control of the excitonic emission states of WS₂, which correlates with the dopant concentration. Such numerical correlation is beneficial as a sensing index for detecting the strength of the nucleobase solution.

Besides, the optical response of another nucleobase guanine on our CVD WS₂ platform has also been observed. based on the comparison under same solution concentration shown in **Figs. 3.4** (b), (c), the adenine and guanine exhibit different effect on PL profile and can be quantitatively distinguished based on their different evolution trend. the PL profile shows different response for adenine and guanine as the calculated I_{A^-}/I_A is 6.930 for guanine and 2.256 for adenine, which means a disparity in electron modulation ability of these two kinds of dopants. This is possibly due to the difference in electron withdrawing ability relative to n-type WS₂ among adenine, guanine, cytosine and thymine, as the previous theoretical work reports less pronounced shift in density of states of WS₂-nucleobase complex in cytosine and thymine cases, indicating their generally less effective reduction in electron density to WS₂ sample [85]. The overall PL responses on our WS₂ platform is summarized as three kinds of responses in four cases, illustrating an acceptable selectivity. To further distinguish cytosine and thymine, more strategies and systems must be explored.

Thus, the 1L CVD WS₂ platform may serve as an alternative optical sensor for nucleobases. Compared to MoS₂, our WS₂ samples yield a much stronger emission [14] and a clear peak splitting with two distinct peaks for the optical signatures of A and A⁻, allowing the precise

fitting of multiple peaks, which is vital for the study of the evolution of excitonic emission. The easy coating procedure on the as-grown sample causes a significant signal change, which is equally effective but much more convenient than previously reported fluorescence labeling approaches [64,74,94]. Furthermore, the detection limit for adenine reaches the micromolar level. Though the sensitivity is not optimized into nM level as in previous fluorescence labeling sensors [64, 74]. With further signal amplification, such as by applying a TMD-gold plasmonic structure [95], the limit may even reach the nanomolar or even picomolar level.

3.3.5 Electrical measurement of WS₂ with adenine coating

Figure 3.5 (a) Optical and (b) Fluorescence images of monolayer WS₂ transistor.

To directly observe the p-type doping effect of the adenine on 1L WS₂, a back-gated field effect transistor was fabricated and measured before and after coating with the adenine solution. **Fig. 3.5** (a) shows an optical image of the 1L WS₂ FET device which was fabricated via a standard electron-beam lithography process. We used a mechanically exfoliated monolayer sample for the devices, which show a clear transport curve profile and offer the opportunity to observe any shifts in the threshold voltage [43]. **Fig. 3.5** (b) is the corresponding fluorescence image of the 1L WS₂ device. The bright fluorescence feature indicates that the monolayer channel persists and remains an intense emission after device fabrication. In **Fig. 3.6** (a), electrical transport curves of the 1L WS₂ device with and without the 0.7 mM adenine solution coating

are shown. As shown by the red curve, the typical drain-source current versus back-gate voltage (I_{ds} - V_{bg}) transport property of the as-fabricated device was measured at a bias voltage (V_{ds}) of 5 V. The result shows an unambiguous n-type behavior. After depositing adenine, as depicted by the green curve, the threshold voltage shifts toward the positive region compared to that of the bare WS_2 device. Such a shift in the threshold voltage and decreased current scale are strong evidence of a reduction in the electron density in the WS_2 sample via charge transfer induced by nucleobase adsorption on the 2D semiconductor surface. This kind of p-type doping is shown in the electrical transport characteristics and is in good agreement with our findings from the optical measurements discussed above.

Figure 3.6 Modulation of transport property and gated PL feature of exfoliated 1L WS_2 with adenine solution coating. (a) I_{ds} - V_{bg} curves under $V_{ds} = 5$ V of the as-fabricated device and the device with the coating of 0.7 mmol/L adenine solution. (b), (c) The Lorentz fitted PL spectra of the as-prepared 1L WS_2 and WS_2 coated with 0.34 mmol/L adenine solution under -35 V and

-5 V gate voltage. (d) The intensity ratio I_{A^-}/I_A and the electron concentration (n_e) of for the WS₂ with/without coating as a function of gate voltage. The straight lines are the linear fitting for I_{A^-}/I_A and n_e with error bars.

To further reveal the effect of adenine on WS₂, especially on the carrier concentration when applying a gate voltage (carrier injection), gate dependent PL measurements before and after coating with the adenine solution were performed (**Figs. 3.6** (b), (c)). Upon applying different gate voltages, a series of shifts in the PL profile were observed. Under each applied voltage, the evolution of the excitonic states caused by the adenine coating was well conserved. As the gate voltage increased, the spectra of the as-prepared and the doped WS₂ transformed differently, which can be attributed to the altered response to the electrical carrier injection. Consequently, an offset in PL feature, parallel to the voltage shift in the I_{ds} - V_{bg} measurement in **Fig. 3.6** (a), was discovered. For example, the PL excitonic feature of pure WS₂ under -35 V is comparable to that of adenine/WS₂ at a voltage of -25 V, indicating a voltage displacement at around 10 V. Within the same framework, we applied the derived I_{A^-}/I_A value and calculated the related n_e to illustrate the p-doping effect of adenine on WS₂ (**Fig. 3.6** (d)). The n_e can be relatively well fit by a linear function for both scenarios. In the adenine/WS₂ case, the fitting residuals are nearly negligible. This proves that our preferred theoretical framework to determine n_e is reasonable, considering the linear carrier-injecting nature of gate doping [6]. The difference in the slope of n_e - V_{bg} indicates a four-fold suppression of carrier injection because of the p-type doping from adenine. These observations reflect the reduction in the electron concentration of the sample.

3.3.6 Universal doping effect of adenine on few layer WS₂ and MoS₂

In addition, we fabricated few-layer WS₂ (**Fig. 3.7** (a)) and MoS₂ devices and observed a similar doping effect in the electrical measurement, indicating the general electron affinity of adenine when attached to layered TMDs. We observed the similar impact of adenine on

electrical property of few layer WS₂ as well, as shown in **Fig. 3.7** (b). Compared to the electrical response of 1L WS₂ device, the few-layer WS₂ device goes through a larger shift in threshold voltage, probably due to the suppression of phonon scattering induced more conductive channels for the electron withdrawing process [96].

Figure 3.7 (a) Optical image of few layer WS₂ transistor. (b) The I_{ds} - V_{bg} transport curve of corresponded WS₂ transistor before and after 0.7 mmol/L adenine solution coating.

The similar p-doping effect of adenine on MoS₂ has been observed for both optical and electrical measurements. As denoted in **Fig. 3.8** (a), the as exfoliated sample yields a PL spectrum which can be clearly fitted into three Lorentz peaks. These peaks are later assigned as A⁻ (1.85 eV), A (1.89 eV) and B exciton (2.01 eV). After adenine attachment the shape of spectrum shows a discernible transformation as the A⁻ component becomes less dominant and A component takes up more majority of the overall PL profile. This excitonic evolution, analogous as in the WS₂ case, can also be attributed to the p-type doping which is directly illustrated in electrical measurement in **Fig. 3.8** (b). Compared to as fabricated device, the threshold voltage shifts to positive region and the device experienced a drop in current scale, vividly demonstrating the reduction of electron in MoS₂ channel. These measurements suggest a general interaction between 2D TMDs and DNA nucleobases, further defending our argument for the WS₂-adenine instance.

Figure 3.8 (a) The decomposed PL spectrum before and after the adenine solution is coated on the MoS₂ sample. (b) The I_{ds} - V_{bg} transport curve of a MoS₂ transistor before and after 1 mmol/L adenine coating.

3.4 Conclusions

Through experiments, we found that WS₂ monolayers exhibit a tunable optical excitonic emission after coating by nucleobases. This phenomenon was further investigated and explained as the result of the charge transfer process generated between the bases and WS₂. Our hypothesis is proven by PL spectra and further supported by the electrical transport measurements. In a typical example, a simple and effective modulation of the excitonic features of monolayer WS₂ was demonstrated via the physisorption of adenine, which should also be applicable to other bases such as guanine and other TMD materials. We believe this is a cornerstone study for the development of future optical sensing, illustrating an alternative way to use TMD materials in biological applications.

Chapter 4 Engineering valley properties of monolayer WS₂ by physical doping

4.1 Introduction and motivation

Layered TMDs semiconductors have been demonstrated to carry the spin-like degree of freedom known as valley pseudospin, which can be optically generated and detected via circularly polarized PL spectra [11,13,44,97]. In specific, this two-fold valley DOF directly corresponds to the optical bandgap of +K and -K valley in the Brillouin zone [9]. Due to strong spin-orbit coupling and broken inversion symmetry, together with time-reversal symmetry, spin and valley DOFs are coupled in monolayer TMDs [16]. This property enables selectively pumping +K (-K) valley with left (right) hand circular light excitations to create an imbalanced carrier population between two valleys. Realizing such net valley polarization is an essential step for developing valleytronic devices [98-102]. Resulted from the opposite selection rules of two valleys, controlling valley polarization in monolayer TMDs by optical helicity is achievable. As experimentally measured, the circular polarization degree (P_c) reflects the population ratio between two valleys which generate light emissions with opposite helicity. Ideally, if photo-excited carriers are fully polarized within single valley, this value should be approaching 100%. However, the reported values of P_c in monolayer TMDs vary from 2% to nearly 100% among different TMD semiconductors [29,103-106], which are mainly attributed to intervalley scattering process from the selectively pumped valley to the opposite one [106-108]. As for the PL measurements, various approaches have been adopted to obtain a sizable P_c , like applying magnetic field, cooling down to liquid helium cryogenic temperature, using near resonant light excitation or building van der Waals heterostructure [11,44,103,109-114]. More practical and desirable methods could be electrical and optical control of valley polarization in TMDs at non-cryogenic temperature and off-resonance conditions. Towards this goal, one of the most effective means is in-situ carrier doping by physical or chemical

approaches [32,43,115]. The introduced resident carriers in TMDs not only tailor the exciton species but are expected to considerably tune the valley polarization dynamics which dominates P_c values as well [116,117]. In previous reports, the changes of valley polarization/relaxation dynamics due to carrier doping have been noticed but haven't been investigated systematically and the mechanism remains elusive [29,111,118,119]. In addition, the unintentional doping and localized states in TMD samples play important roles to influence their optical properties, which may lead to discrepancies in experiments using layered TMD samples with different initial electronic states [45,120]. Therefore, probing correlations between valley polarization and carrier concentration is crucial for future manipulations and potential applications based on valleytronic properties in TMD samples prepared by mechanical exfoliation or chemical vapor deposition (CVD) with various native and/or external carrier doping from environment.

4.2 Experimental details

4.2.1 Sample preparation and Device Fabrication

Commercial WS₂ crystal (2D semiconductors Inc.) was mechanically exfoliated onto highly doped 300 nm thick SiO₂/Si wafer. For the device fabrication, the drain/source electrodes were made of 5/80 nm of Cr/Au by thermal evaporation and after standard electron beam lithography (Oxford SEM system) and the lift-off process. Before the gated PL measurements, the device was wire bonded to a PCB board.

4.2.3 In-situ PL measurements with physical doping

Micro-PL measurements were performed using a WITec Raman system with excitation wavelengths of 532 nm through 50 × objective lens. As for the circular polarization resolved PL, a quarter wave plate was inserted along incident light to convert the linear polarized laser into circular polarized light. Besides a linear polarizer was inserted along the emission light

before CCD collection to filter the emission light with left/right helicities. We used 600 lines/mm grating for PL measurements. For gate-dependent PL measurement the sample was loaded in the Linkam stage and connected with a Keithley 4200-SCS semiconductor characterization system to apply gate voltage between Si substrate and the source/drain electrode, at 80 K in high vacuum (10^{-3} mbar). The excitation power was kept at 40 μ W (5.09 kW/cm²) for gate dependent circularly polarized PL measurement.

4.3 Results and discussion

4.3.1 Monolayer WS₂ based platform and valley polarization

Polarization-resolved PL measurements of the mechanically exfoliated monolayer WS₂ were conducted under excitation from a σ^+ circular polarized 532 nm (2.33 eV) laser and filtered with σ^+/σ^- helicity to measure the emission from +K/-K valley (**Fig. 4.1**). The polarization degree P_c is calculated by the equation:

$$P_c = \frac{I(\sigma^+) - I(\sigma^-)}{I(\sigma^+) + I(\sigma^-)} \quad (4-1)$$

where $I(\sigma^\pm)$ denote the left/right hand circular polarization resolved PL intensity. Based on optical selection rule, σ^+ (σ^-) excitation solely couples to excitonic transitions in the +K (-K) valley and the light emission should carry single handedness. However, as schematically shown in **Fig. 4.1** (b), when the +K valley is selectively pumped with σ^+ excitation, the resulted PL light emission contain not only σ^+ signal from polarized excitonic transitions in +K valley but also σ^- signal due to intervalley scattering of excitons from +K to -K valley [18]. The overall circular polarization degree P_c is determined by equation:

$$P_c = P_0 / (1 + 2 \tau_0 / \tau_v) \quad (4-2)$$

where P_0 is initial polarization, τ_0 is the valley exciton decay time, and τ_v is the intervalley relaxation time. The term τ_0 / τ_v indicates that the value of P_c largely depends on the competition between two processes: radiative recombination of valley polarized excitons and

intervalley scattering. While τ_v (intervalley scattering dynamics) can be significantly tuned by screening effect induced by carrier doping, which will be discussed in detail later. **Fig. 4.1** (c) shows PL spectra from a field effect device of exfoliated 1L-WS₂ measured at room temperature (RT) and 80 K. Generally, the PL spectra consists of two components, where the high/low energy peak corresponds to neutral exciton (A)/negative trion (A⁻) emission [32]. At low temperature the A and A⁻ peaks present a blue shift which has also been observed in MoS₂, MoSe₂ and CVD WS₂ recently [14,121]. The two exciton peaks are well resolved at various carrier concentration, which enable us to perform the multiple-peak fitting properly and study the evolution of these exciton species separately.

Figure 4.1 Monolayer WS₂ based device to explore the doping dependent valley relaxation dynamics. Schematic image of: (a) experimental set up for circularly polarized PL at various carrier densities, (b) optical selection rules at +K/-K valleys and intervalley scattering process. (c) Polarization resolved PL spectra with both σ^+ / σ^+ configuration at room temperature and 80 K.

4.3.2 Gate voltage dependent valley polarization of monolayer WS₂

Fig. 4.2 (a) shows PL features from a field effect device of exfoliated 1L-WS₂ with the back-gate voltages from -55 V to 55 V. Overall, two components A and A⁻ in emission band are well identified. Their corresponding photon energies and spectra dominance change as the voltage sweeps. At gate voltage below -15 V, both A and A⁻ features are visible. While at higher gate

voltage, the integrated intensity of A peak gradually decreases and A⁻ peak becomes dominated due to the electrostatic doping, resulting in a single peak profile at higher carrier density. In addition, the peak position of A blueshifts and that of A⁻ redshifts, which leads to the increase of energy difference between A and A⁻ (i.e. dissociation energy), as can be directly seen in **Fig. 4.2 (b)**. This is attributed to phase space blocking due to Pauli exclusion and many-body effects [122]. As the gate voltage sweeps from negative to positive, the A⁻ emission energy redshifts by roughly 21 meV. The dissociation energy also monotonically increases to around 50 meV from gate voltage of -55 to -15 V. These behaviors agree well with the previous experimental reports on natively N-doped TMDs like MoS₂ and WS₂ [32,36,84]. The maximum external doping level is estimated as $\Delta n = 7.69 \times 10^{12} \text{ cm}^{-2}$ at 55 V gate voltage compared with -55 V, as discussed later in **4.3.3**.

Helicity resolved PL spectra from p-type (-45V) and n-type (+55 V) gated sample are shown in **Fig. 4.2 (c)**, respectively. When the WS₂ is negatively gated, A⁻ shows a low polarization degree of 7%. While, at a positive gate voltage and a higher induced carrier density, the sample exhibits a single A⁻ peak and a drastically higher polarization degree of 25%. The evolution of polarization degree as a function of gate voltages is shown in **Fig. 4.2 (d)**. As an indicator of the electron density, the integrated intensity ratio of A⁻ to A is illustrated at lower carrier concentration regime where the neutral exciton A is visible. The increment of this ratio indicates elevated electron density [37,42,120]. Obviously, as the voltage is swept from -55 V to +55 V, the polarization of trion is enhanced by more than three-fold.

The external doping level is estimated in electrostatic doping scenario, by converting the gate voltage to the electron doping density ($ne = CV_g$), the back-gate capacitance of is determined by $C = \epsilon_0 \epsilon_r / d$ while $\epsilon_0 = 8.85 \times 10^{-12} \text{ Fm}^{-1}$, $\epsilon_r = 3.9$, $e = 1.6 \times 10^{19} \text{ C}$, $d = 300 \text{ nm}$, then $c = 1.12 \times 10^{-8} \text{ Fcm}^{-2}$, with 110 V voltage difference, we estimated $\Delta n = 7.69 \times 10^{12} \text{ cm}^{-2}$. Another benchmark for electron doping is tunable Fermi energy $E_F =$

$\hbar^2\pi n/2m_e e^2$. The dissociation energy obeys $E_A - E_{A^-} = E_{TB} + E_F$, where E_{TB} is the trion binding energy. It designates that the dissociation energy increases linearly with electron doping Δn , which is proportional to voltage difference or excitation power. As mentioned in main article, the ratio I_{A^-}/I_A also reflects the electron density $n \sim I_{A^-}/I_A \times 10^{11} \text{ cm}^{-2}$ [29, 32]. Note that at -55 V gate voltage we estimated the initial carrier density $n_0 \sim 0.5 \times 10^{11} \text{ cm}^{-2}$. In **Fig. 4.4**, these benchmarks in σ^+ and σ^- emission are identical as the electron density increases.

Figure 4.2 Gate voltage dependent circularly polarized PL measurement of monolayer WS₂. All optical excitation is right circularly polarized (σ^+). The exciton species and corresponded polarization degree values are labeled, respectively. (a) PL intensity mapping (color scale in counts) of monolayer WS₂ as a function of gate voltage and photon energy, with σ^+ detection. (b) Corresponding Photon energies of A and A⁻ excitons (left vertical axis) and dissociation

energy of A^- (right vertical axis) versus gate voltage. (c) Polarization resolved PL spectra of gated WS_2 , both with σ^+ (σ^-) detection at 80 K. (d) Intensity ratios I_{A^-}/I_A (left vertical axis) and A^- circular polarization degree (left vertical axis) measured in as-exfoliated 1L WS_2 versus gate voltage. The error bars correspond to standard errors of peak heights in multiple peak fittings.

Compared to the previous reports [104,123], the overall P_c value especially at lower doping level is relatively low, potentially attributed to that off-resonance laser excitation produces a large detuning energy ~ 0.3 eV and temperature is far above typical helium cryogenic temperature (4-10 K), which leads to lower initial polarization (P_0) [108,124]. More detailed discussion of P_0 is shown in following parts.

Figure 4.3 Correlation among carrier density concentration, the valley relaxation time and temperature for monolayer WS_2 . The dashed (solid) lines corresponds to the relaxation time in the (thermal) collisional broadening regime. Adapted from Ref. [129].

4.3.3 Theory of carrier screening effect on intervalley scattering process

The enhancement obtained in this work is attributed to carrier doping induced suppression on valley relaxation process. The intervalley scattering process of exciton is governed by electron-hole exchange interaction through the Maialle-Silva-Sham mechanism, resulting in short valley

lifetime in picosecond scale [125-127]. In the previous studies by electrically tailoring the doping states in graphene, the intervalley scattering rate was strongly suppressed [128]. This carrier doping approach was proposed to be applicable to other multivalley systems like TMDs. Furthermore, as indicated by a comprehensive theoretical study on WS₂ recently [129], valley exciton relaxation time (τ_v) correlates with carrier concentrations and temperatures (**Fig. 4.3**). This framework is quantitatively compared with our experiment results. In this work we are trying to manipulate the τ_0/τ_v value by tuning electron doping and then to tailor the P_c value consequently. In regards of the electron doping effect on τ_v , the previous mentioned framework suggests in both collisional and thermal broadening regimes, the value of τ_v shows maximum discrepancy (~6-fold) versus carrier concentration at around 70-90 K [129]. This implies the intervalley scattering process can be effectively suppressed by carrier doping at liquid nitrogen temperature (i.e. 80 K). Compared to τ_v , τ_0 is much less affected by carrier doping, as discussed in 4.3.6. Consequently, the τ_0/τ_v and P_c values are considerably tuned by electrostatic doping, which agrees well with our experimental observations. This is of great importance for the circularly polarized PL study at liquid nitrogen temperature. The physical doping effect is further illustrated by following experiments.

Figure 4.4 Additional information from circularly polarized PL measurement of monolayer WS_2 as function of gate voltage. All optical excitation is right circularly polarized (σ^+) with σ^+ and σ^- detection, respectively. The exciton species are labeled. (a) PL intensity ratios of I_{A^-}/I_A for monolayer WS_2 versus gate voltage. (b) Integrated intensity of A^- exciton with σ^+ and σ^- detection versus gate voltage. (c) Full width at half-maximum (FWHM, i.e. PL linewidth) of A and A^- excitons versus gate voltage. (d) Emission energy of A and A^- excitons with σ^+ and σ^- detection versus gate voltage.

4.3.4 Power dependent valley polarization of monolayer WS₂

As reported in graphene [130] and TMDs [32], in addition to electrostatic doping, the carrier concentration can also be modified by light excitation, which not only creates electron–hole pairs, but dynamically ionizes the carriers trapped on the donor impurities levels toward conduction band as well [32]. Here, we studied the influence of excitation laser power on the circularly polarized PL emission of 1L WS₂ at 80 K. **Fig. 4.5** (a) shows the intensity mapping of PL spectra at various excitation power, in σ^+/σ^+ configuration. Like electrostatic doping case (40 μ W excitation, -55 V to 55V), the overall PL profile evolves from the two-peak (A and A⁻) feature into a single peak (A⁻) feature at increasing excitation powers. The corresponding photon energies and integrated intensities versus power are depicted in **Fig. 4.5** (b). Identical to electrostatic doping case, as power increases within 600 μ W, the A exciton peak slightly blueshifts while the A⁻ exciton peak redshifts, which are signatures of photoinduced electron doping [29,32,131].

With regards to the optical doping dependent valley polarization, as shown in **Fig. 4.5** (c), the P_c value of A⁻ shows great distinction at weak (1.72 μ W, corresponding to 0.219 kW/cm²) and strong (1754 μ W, corresponding to 223.32 kW/cm²) excitation regime. Note that here we use laser power as a measure of excitation strength. In details, three folds enhancement of P_c from 7% to 22% is achieved with power increasing from 1.72 μ W (0.219 kW/cm²) to 3930 mW (500.38 kW/cm²). The completed power dependence of P_c is plotted in **Fig. 4.5** (d). Compared to the gate voltage dependence, there is pronounced fluctuation rather than monotonical increasing, especially at higher powers in mW scale. At both low and high powers, the carrier doping induced screening effect is prominent to influence valley polarization.

Figure 4.5 Power dependent circularly polarized PL measurement of monolayer WS₂. (a) PL intensity mapping (color in counts) of monolayer WS₂ as a function of excitation power and photon energy, with σ^+ detection. Note that the intensity and power are in log scale. (b) Corresponding Photon energies of A and A⁻ excitons (left vertical axis) and dissociation energy of A⁻ (right vertical axis) versus power. (c) Polarization resolved PL spectra of WS₂ pumped at different powers. (d) Circular polarization degree, (e) A⁻ line width and (f) integrated intensity

of trion peak measured in 1L WS₂ at various excitation power. Solid lines are linear fitting curves on log-log scales and α values correspond to the slopes. The error bars correspond to standard errors of peak heights/widths in multiple peak fittings.

At low optical excitation ($<532 \mu\text{W}$ i.e. 67.73 kW/cm^2), the overall effect of photo induced electron doping is clearly demonstrated, which is comparable to our observation in the gate dependent PL measurements. In details, it is noticed that the dissociation energy between A and A⁻ at various power shift in the same manner as the electrostatic gated sample. Under the excitation of $373 \mu\text{W}$ (47.49 kW/cm^2), the observed dissociation energy is as large as around 0.05 eV , equivalent to doping effect of 40 V voltage difference (from -55 V to -15 V) and electron density increase is estimated as $2.79 \times 10^{12} \text{ cm}^{-2}$. Importantly, the electron doping effect on valley relaxation is witnessed in the evolution of P_c values. In this regime the P_c value is increased from 7% to 15% . This 2-fold enhancement stay in line with our electrical doping results within 50 V difference and indicates the τ_0/τ_v is effectively tailored.

At higher powers from 532 to $3930 \mu\text{W}$ (67.73 to 500.38 kW/cm^2), however, the P_c value become more diverged with a weak increasing trend up to 22% at $1754 \mu\text{W}$ (223.32 kW/cm^2). The power dependence of A⁻ integrated intensity ($I_{\text{Total}} = I_{\sigma^+} + I_{\sigma^-}$) is depicted in **Fig. 4.5** (e). The intensity shows linear relationship with excitation power and a slope of ~ 1.05 at power less than $532 \mu\text{W}$ then saturated with a slope of 0.34 . This first slope value presents a symbol of A and A⁻ exciton emission [29,32]. Noticeably, at higher power the A⁻ peak experiences obvious broadening from 44 to 57 meV caused by excitation induced dephasing effect (**Fig. 4.5** (e)) [132]. This is in sharp contrast with the electrical doping case where the A⁻ exciton linewidth is relatively unchanged at various gate voltages (**Fig. 4.4** (c)). Note that the excitonic linewidth is a partial reflector of coherence lifetime, which is influenced by intervalley scattering [133,134]. Theoretically, this PL linewidth is proved to be inversely proportional to the τ_v term when temperature and doping level are fixed (**Chapter 4.3.5**) [129,132]. As

consequences from accelerated intervalley scattering, excitation induced broadening reflects that the further increment of τ_v is hampered. It compromises the enhancement of P_c compared to electrostatic doping case at similar electron density. We applied previous mentioned framework to estimate the P_c with different electron density and PL peak width and got reasonable results which agree well with experimental data range as discussed later. Other potential effects like many-body effects and intravalley depolarization are also discussed (**Chapter 4.3.5**). Overall, these results indicate a 3-fold enhancement of P_c by pure optical excitation, without requirement for device fabrication. Our findings also serve as a reference to the future TMDs based valley polarized PL or photodetector [101] studies conducted at different excitation powers.

4.3.5 Estimation of doping dependent valley polarization

First, we refer to previous established framework to estimate the initial polarization P_0 in our measurements. As the valley relaxation time τ_v is dependent on doping and exciton peak linewidth [129,132]. In specific at finite doping ($> 0.5 \times 10^{11} \text{ cm}^{-2}$), the τ_v can be simplified as:

$$\tau_v = \frac{\hbar}{AJ^2} \frac{K_{TF}^2}{\Gamma} \quad (4-3)$$

where A is a material-dependent constant, J is strength of exchange interaction, $\hbar$ is Planck's constant divided by 2π . While K_{TF} is Thomas–Fermi wave vector which can be further expressed as $K_{TF} = K_0[1 - \exp(-E_F/K_B T)]$. The magnitude of this term rises along E_F which corresponds to electron doping in WS_2 . Γ is the excitonic linewidth, which is inversely proportional to momentum relaxation time. Then tailoring the E_F is a deterministic approach to alter τ_v . While the Γ evolution also reflects that the intervalley scattering is modified by excitation induced fluctuation of valley relaxation dynamics [132].

In electrostatic doping case we estimate P_0 by substitute different τ_0/τ_v governed by above mentioned framework into our experimental measured P_c values. Based on **Eq. (4-2)**

$$P_c = P_0 / (1 + 2 \tau_0 / \tau_v)$$

We roughly subtract the $\frac{\tau_0}{\tau_v}$ values at low and high electron densities from Ref. [130] to derive

P_0 . Note that we assume τ_0 does not change significantly with electron doping.

$$\begin{cases} P_0 / (1 + 2 \tau_0 / \tau_{vhigh}) = 25\% \\ P_0 / (1 + 2 \tau_0 / \tau_{vlow}) = 7\% \\ \tau_{vhigh} / \tau_{vlow} \cong 6 \end{cases} \quad (4-4)$$

Then P_0 can be calculated as 51.4%. Then we adopted this value to predict P_c with corresponding excitation powers. Compared to the electrostatic doping case, optical excitation yields the lower P_c at comparable doping level. This indicates change in E_F not enough to explain the observed P_c evolution. By comparing experimental change of dissociation energy where 337 μW correspond to 40 voltage difference, we can extrapolate the related power values. Referring the electron density at $n_1 = 8 \times 10^{12} \text{ cm}^{-2}$, $n_2 = 4 \times 10^{12} \text{ cm}^{-2}$, $n_3 = 2 \times 10^{12} \text{ cm}^{-2}$, we select $P_1 = 926 \mu\text{W}$ (117.89 kW/cm^2), $P_2 = 463 \mu\text{W}$ (58.95 kW/cm^2), $P_3 = 231.5 \mu\text{W}$ (29.47 kW/cm^2), respectively. As shown in **Fig 4.6** (a), the peak widths are also extrapolated as $\Gamma_1 = 0.05484 \text{ eV}$, $\Gamma_2 = 0.05322 \text{ eV}$, $\Gamma_3 = 0.04921 \text{ eV}$. Then we combine **Eq. (4-3)** and **Eq. (4-4)** to estimate the P_c values upon optical doping. The results are shown in **Fig. 4.6**, the estimated values are in line with our experimental findings, which means the framework we use based on electron doping and PL linewidth broadening is reasonable.

Figure 4.6 Power dependent circularly polarized PL measurement of monolayer WS₂ with estimated data. (a) A⁻ linewidth at various excitation power and estimated widths. (b) Measured and estimated P_c of trion peak in 1L WS₂ at various excitation power.

4.3.6 Disclaimer of valley polarization analysis in monolayer WS₂

Unlike the ideal case [16], P_0 is less than 1 due to defect assisted exciton trapping [135] and ultrafast relaxation of hot excitons [136], and worth for more detailed discussion. The value of P_0 is mainly dependent on the detuning energy, which is the energy difference between excitation laser and A exciton emission [106,108]. It is worth noting that the possibility of P_c enhancement being determined by the change of detuning energy is ruled out, because as the electrical/optical doping increases, the A⁻ emission energy goes through red shift, which enlarges the detuning energy and may slightly reduces P_0 rather than increases it [106]. In regards of the P_0 value, while some studies treated P_0 as 1 for simplicity [137], previous time resolved PL has measured $P_0 = 0.7 \pm 0.1$ in monolayer WSe₂ system with around 150 meV detuning energy [132]. As has been theoretically pointed out [129], the change of τ_v is around 6 times at 80 K when the carrier concentration is tuned from $8 \times 10^{11} \text{ cm}^{-2}$ to $8 \times 10^{12} \text{ cm}^{-2}$, which relatively corresponds to our previously estimated doping state ($\Delta n = 7.69 \times 10^{12} \text{ cm}^{-2}$). We substitute the experimentally measured P_c and corresponding τ_0/τ_v values at

low and high doping into **Eq. (4-2)** to estimate the value of P_0 , which is 51%. Due to the 300 meV detuning energy, the limited value below theoretical limit is consistent with the previous reports [104,138]. Though, via intentional doping, the measured valley polarization P_c can be engineered to approach P_0 , yielding an acceptable value even under off-resonance excitation.

Figure 4.7 Polarization degree of A^- exciton of monolayer WS_2 calculated with different types of PL intensities. (a) Two types of A^- exciton P_c versus gate voltage and (b) excitation power. Power is depicted in log scale.

In regards of optical doping, the constant slope at low excitation regime also indicates that the radiative efficiency which is largely dependent on τ_0 is relatively stable at low excitation power. This makes tuning P_c and τ_v by optical excitation feasible.

As the power continues to go up to mW range, beyond the carrier screening effect in valley relaxation process induced by optical gating effect, enhanced many-body effects at higher exciton densities like exciton-exciton annihilation may also play a role [139,140], supported by a deviation from original slope in power dependence (**Fig. 4.5 (f)**). While some previous time resolved spectroscopic studies indicate higher density of excitons are supposed to mediate depolarization by intravalley exciton-exciton exchange interaction [141]. As consequence of these effects both τ_0 and τ_v decreases at higher power densities, making the evolution of τ_0/τ_v less monotonical. More systems and experimental techniques are required to separate these

phenomena from carrier screening effect. Potential heating effect is also excluded. As the power increases, A exciton peak goes through a blueshift. This presumably excludes the potential laser induced heating which causes the redshift of exciton photon energy.

Figure 4.8 Polarization degree of A exciton of monolayer WS₂ as function of doping. (a) P_c of A exciton versus gate voltage. (b) P_c of A exciton versus excitation power. Power is depicted in log scale. The error bars correspond to standard errors in multiple peak fittings.

Note that in this study, we focus on intervalley scattering of the bright excitons (trions) between +K and -K valleys. Though dark excitons are reported to preserve robust valley polarization which may also promote P_c [142], it requires in-plane magnetic field [35] or light propagation [143] to effectively visualize these exciton species in PL. For the P_c calculation, as I denotes PL intensity, previous studies have adopted integrated (i.e. exciton peak area) [132,144] or absolute (i.e. exciton peak height) PL intensities [11,12,145]. We have calculated the P_c values using both methods, as shown in **Fig. 4.7**. The overall P_c evolutions with increasing gate voltage or excitation power are identical. In main article we adopt absolute PL intensity for calculation. As for the doping dependence of neutral A exciton, despite very limited data points due to A exciton vanishing with increasing doping, no significant change of P_c has been observed. One possible reason is that the being neutrally charged, A exciton is less

sensitive to the screening field during intervalley scattering process (**Fig. 4.8**). More system need to be exploited to uncover the valley dynamics of A exciton upon doping in future studies.

Figure 4.9 Gate dependent A^- exciton polarization degree of monolayer WS_2 at 300 K and 80 K.

Last, we compare our result with the previous reports on tailoring P_c in exfoliated monolayer WS_2 . Recent magneto PL study has demonstrated valley Zeeman splitting and monotonically increasing P_c of trion emission with applied magnet field in out-of-plane direction [144]. Compared to magnetic methods, electrical/optical control of valley states are more favored for future valleytronic devices operations. As a more practical method to create population imbalance between two valleys, our approaches correspond to a 10 T magnetic field which enhances polarization degree of trion emission from neglectable value to about 25% at 4.2 K [144]. For PL without magnetic field, Cui *et al.* reported $P_c = 40\%$ at near resonance excitation (2.088 eV) and 16% at off-resonance excitation (2.331 eV), measured at 10 K. Korn *et al.* reported 21% for singlet trion and 34% for triplet trion with 2.15 eV laser excitation at 4.5 K [146]. It is clear that we boost the P_c of monolayer WS_2 to a decent value (24% for electrical doping, 22% for optical doping) comparable to the previous achieved ones with much more demanding facilities (**Fig. 4.10**). The gate voltage dependent circularly polarized PL at room

temperature (300 K) is also performed (Fig. 4.9), the obtained values are neglectable without clear trend compared to the doping dependent data at 80 K. This is attributed to reduced τ_v [105] and suppressed tunability by electron doping [129] at higher temperature range.

Figure 4.10 Comparison with previous report on circularly polarized PL measurement of monolayer WS_2 . Black dots denote the previous reported P_c values in Ref. [104] and Ref. [144]. Red (blue) dots represent P_c from our work with and without physical doping at 80 K (300 K).

4.4 Conclusions

In summary, we have studied the valley polarized excitonic emission of monolayer WS_2 . By changing the gate voltage and the excitation power, doping tunable polarization degree in trion emission is achieved. The correlation between electron doping, exciton linewidth and valley polarization are clearly demonstrated in our measurements. In electrical doping case the increasing P_c is mainly attributed to doping induced screening effect, while in optical doping case, especially at higher excitation powers in mW scale, not only the screening but also peak broadening effect is needed to be taken into considerations to explain the spectra features and P_c evolution. These findings serve as a reference for future valleytronic studies using TMD

samples with different native or extrinsic doping level. Furthermore, based on our discovery of carrier screening effect, chemical doping or heterostructure formation are also expected to affect the valley polarization of A excitons in TMDs, which is promising for non-degenerate P_c engineering. Our studies develop a simple but practical strategy for electrical and optical control of the valley polarization state, which is a corner stone for future noncryogenic valleytronic operations.

Chapter 5 Deterministic isolation of bound exciton luminescence in 2D semiconductor nanodisks

5.1 Introduction and motivation

Monolayer transition metal dichalcogenide semiconductors have gained tremendous attention for their unique optical properties, such as direct bandgap at +K/-K valley which couples to the carrier spin [9,11,21,44], robust exciton and trion emission [36] which are sensitive to biochemical molecular doping [43,115], possibilities to probe many-body [32,120] and valley [147-149] physics, and great potential in optoelectronic applications as novel photodetector [101], electroluminescence light source [102] and lasing [150].

Furthermore, recently single-photon emitters [33,34,151,152] have been found in the TMD semiconductors, which could serve as a cornerstone for quantum information and communication applications at visible to near infrared wavelength [153]. Generally, these narrow emitters result from exciton trapped in defect potentials which can be tuned by strain gradient [154]. However, these native quantum emitters in TMDs are scarcely found on sample, and the wavelengths of emission modes are diversely distributed across the broad defect emission region, creating dozens of undistinguishable narrow peaks. Such low yield as well as random spatial and spectral positioning of the emitters do limit their further developments. To overcome these obstacles, efforts have been devoted to developing artificial emitters mainly based on defect [155] and strain engineering [154,156-159]. Unfortunately, most of these approaches require complicated fabrication process to prepare pre-patterned metal nanorods or silica nanopillars. In addition, to introduce strong perturbation, tip scratching [159] or extreme deformation created by nanopillars [158] may damage the sample. Therefore, a non-invasive method is desired to produce the regulated, high-yield TMD emitters without requirement of substrate engineering. It is an essential start to introduce lateral dimension confinement to a

sample itself, which should be able to manifest the defect trapped exciton emission of TMD layers and deterministically isolate these narrow PL peaks.

The major principle of creating artificial emitters previously is through strain engineering. By suspending the sample [154] or introducing point-like perturbation by nanopillars (150 nm in diameter) [158], localized strain is effectively introduced to the sample. As a result, the potential landscape of strained region evolves accordingly and trap the randomly distributed localized excitons, forming spectrally distinguishable emitter-like peaks without energy overlapping [160,161]. In addition to applying external force, it has been proposed that the intrinsic localized strain (2% to 4% tensile strain) exists along the edges of natural TMD flakes [162]. This strain effect correlated with defects at edges is a potential reason to explain why most spectrally isolated narrow defect emission centers were found along the edges and interfaces between multilayer and monolayer regions [34]. As the dimension goes down, the perimeter to area ratio ($\sim \pi d / \pi d^2$, d denotes disk diameter) increases, therefore such edge emission could dominate the entire monolayer, which can be visualized by PL measurements in our experiments. Here for the first time we demonstrate a fresh strategy, achieving such strain induced luminescence confinement to the as-prepared TMD monolayers, via fabricating sub- μm nanopatterns with precise dimension control.

5.2 Experimental details

5.2.1 Sample preparation

CVD WS_2 flakes were grown onto highly doped 300 nm thick SiO_2/Si wafer based on CVD method reported previously [45]. NaCl was mixed with WO_3 powder to promote the growth of large flakes [47]. Commercial WSe_2 crystal (2D semiconductors Inc.) was mechanically exfoliated onto same type of SiO_2/Si wafer substrates. Then the nanodisks were patterned by EBL, followed by Ar plasma etching process.

5.2.2 Optical characterization

The fluorescence images were captured by an Olympus microscope with a Mercury lamp as the excitation light source. At 4.2 K, the PL spectra were measured with a custom-designed confocal micro-PL spectroscopy/image system (attocube). The excitation laser source is continuous-wave laser of 532 nm with a power less than 150 μ W unless indicated otherwise. At higher temperatures from 80 K to 220 K, micro-PL and Raman measurements were performed using a WITec confocal Raman system with excitation wavelengths of 532 nm through 50 $\times$ objective lens. The sample was sealed in Linkam stage in high vacuum (10^{-3} mbar). As for the circular polarization resolved PL, a quarter wave plate was inserted along incident light to convert the linear polarized laser into circular polarized light. Besides a linear polarizer was inserted along the emission light before CCD collection to filter the emission light with left/right helicities. We used 600 (1800) lines/mm grating for PL (Raman) measurements. The linear polarization resolved PL was conducted by same system without quarter wave plate.

5.3 Results and discussion

5.3.1 Comparison between PL from WS₂ nanodisks and flakes

Our WS₂ nanodisks are fabricated by a top-down method based on CVD [14,45,47] grown large WS₂ flakes with bright PL emission on SiO₂/Si substrate. As schematically shown in **Fig. 5.1 (a)**, we used electron beam lithography to fabricate the designed pattern with controlled size and shape, the photoresist functions as masks during following plasma etching process (**Fig. 5.1 (b)**). The product is shown in **Fig. 5.1 (c)**, with fluorescence image of nanodisks and continuous flake regions used for control measurements. The inset scanning electron microscopy (SEM) image shows clearly that sub- μ m size nanodisks are obtained. The PL spectra of the nanodisk relative to the continuous flake emission at room temperature (RT) is evident in **Fig. 5.1 (d)**.

Figure 5.1 (a) Schematic image of transforming WS₂ flakes into nanodisks. (b) Optical image of WS₂ flake with PMMA mask. (c) Florescence image of as-fabricated WS₂ nanodisks, inset is the SEM image of single nanodisks, the corresponding scale bar is 1 μm. The PL spectra of WS₂ nanodisk and flake at (d) room temperature and (e) 4.2 K.

Compared to flake which shows typical PL spectra of CVD WS₂ [45,115], the PL of nanodisks displays obvious blue shift. The detailed fitted spectra are shown in **Fig. 5.4** (a). Compared to the flake region, A exciton is blue shifted for around 27 meV in PL of nanodisk at room temperature. This energy shift is in similar amount of blueshift induced by 2.5% uniaxial strain

in WS₂ [61], though here the strain direction based on circular geometry should be identical to previously reported suspended sample, which is anisotropic [154]. Despite the difference of strain type, similar energy shift has been observed in other strain engineered artificial emitters, which supports the existence of localized strain in our nanodisks [154]. When the temperature is cooled down to 4.2 K, as shown in **Fig. 5.1** (e), the PL of flake region shows typical spectral features of CVD grown WS₂, with defect bound exciton dominating the broad spectral range and vague A exciton and trion features [32]. These PL features are common in the WS₂ flake regardless of location. In sharp contrast, the representative PL of the nanodisk (~300 nm diameter) demonstrates the sub-nm PL peaks, which are well isolated from original broad defect band emission. Such evolution is attributed to the strain induced modulation of potential landscape of the 2D excitons, which potentially guides randomly distributed localized excitons within broad wavelength regions to funnel into narrow spectral regions, as examined in detail in following parts [160,161,163]. This is further evidenced by the evolution of PL spectra of the nanodisks with various sub- μm diameters, which display emerging of narrow bound exciton emission at 4.2 K (**Fig. 5.2**) and blueshift of A exciton at higher temperatures (**Fig. 5.4**).

Figure 5.2. (a) Fluorescence image of as-fabricated WS₂ nanodisks. (b) PL spectra of WS₂ nanodisks with different diameters at 4.2 K. (c) PL spectra of WS₂ nanodisks with same designed diameters at 4.2 K. (d) Distribution of the sub-nm peak emission wavelengths and (e) linewidths measured for A series nanodisks. (f) The evolution of spectral range as the WS₂ size decreases.

5.3.2 Size dependent evolution of defect bound exciton emission of WS₂ nanodisks

To systematically reveal the necessary size to confine the excitons and promote the isolated emitter-like PL peaks, we performed PL measurements on nanodisks of various diameters. As shown in **Fig. 5.2** (a), the disks with label A to E correspond to the diameter from 300 to 1460 nm, accordingly. Within the same line, the disks are designed with identical diameters. The PL feature at 4.2 K is shown in **Fig. 5.2** (b), the size dependent PL evolution is clearly visualized. As the disk diameter scales down, especially in sub- μm range, the isolated narrow peaks gradually emerge from broad emission without distinguishable emitter features (**Fig. 5.3**), as a result of increasing localized strain, which is supported by shift of A excitons in PL at higher temperatures (**Fig. 5.4**). The PL spectral range is also reduced from ~ 70 nm in flake to ~ 18 nm in A series nanodisks (**Fig. 5.2** (f)). With the same programmed diameters ($\sim 300 \pm 50$ nm), the formation of narrow defect exciton emission is highly reproducible as shown in the PL spectra in **Fig. 5.2** (c). The representative PL features of A1 to A4 disks demonstrate discernable, well resolved defect bound exciton peaks within narrow spectral range.

Figure 5.3. Fitted representative PL spectra of (a) A2 and (b) A4 disk at 4.2 K. The narrow peaks are labeled with corresponding linewidths.

To further demonstrate that our approach is deterministic, **Fig. 5.2** (d) plots a statistic of the wavelength of sub-nm peaks, which are extracted from over 30 typical PL spectra of A series

nanodisks. More than 80% of peaks are located within 610 to 616 nm, indicating precise spectral positioning. Among these peaks 86% have linewidth of 0.7 to 1 nm (**Fig. 5.2 (e)**). This control of emission wavelength is relatively better than previous nanopillar based emitters [157,158], which present ~70% of sub-nm emission peaks within 620 to 640 nm for WS₂ and a spread distribution across 720 to 800 nm for WSe₂. In the sense of quantum information, realizing accurately positioned emitters with determined wavelengths is a first step towards scalable manufacture and on-chip integration of quantum devices which transmit signal at relatively consistent frequency. The wavelengths of our emission modes are consistent with previous confirmed monolayer WS₂ single photon emitters [158], which denotes the type of our engineered defects are suitable for quantum emission.

Figure 5.4 (a) The fitted PL spectra of WS₂ nanodisk and flake at room temperature. PL spectra of WS₂ nanodisks with different diameters at (b) 220 K, (c) 170 K, and (d) 80 K.

Interestingly, at 80 K the circular/linear polarization resolved PL on nanodisks (300 nm diameter) exhibit novel polarization property of confined defect bound exciton, which is distinct from the A exciton polarization (**Fig. 5.5**) and previous reports on valley coherence of TMDs [119]. In specific the bound exciton yields high (83%) linear polarization ($P_L = \frac{I(H)-I(V)}{I(H)+I(V)}$) with neglectable circular polarization ($P_C = \frac{I(\sigma^+) - I(\sigma^-)}{I(\sigma^+) + I(\sigma^-)}$) even at off-resonance excitation (2.33 eV). One potential explanation is that the in-plane exciton dipole interacting with anisotropic strain at emitter location [164]. This linear polarization of localized exciton agrees well with identified TMD single photon emitters [33,159], suggesting another prerequisite towards quantum light source generation.

Figure 5.5. (a) Circular and (b) linear polarization resolved PL spectra of 300-nm WS₂ nanodisk at 80 K.

Note that for the mechanism of size dependent PL evolution, we conclude that the etching induced formation of nanocrystallites [51] along the edges or quantum confinement of A exciton [53] are not likely to play a dominate role here. We have two supports to exclude the major role of etching induced nanocrystallites. First evidence is that the distinct size dependent PL spectra are found sample wide, rather than showing identical spectra features only at edges

of both disks. The second reason is that though the etching induced rich defects or nanocrystallites with various domain sizes may also promote the localized exciton emission, they are hard to control precisely and could not lead to deterministic generation of narrow peaks at unified emission wavelength, without the help of local strain gradient [154,161]. Moreover, the shift of A exciton emission energy should not be attributed to quantum confinement, either, as the lateral dimension of our disks (as small as 300 nm diameter) are still much larger than screening length of excitons (7.5 nm) [26], unlike the previously reported monolayer quantum dots case [53].

5.3.3 Large-scale WS₂ nanodisk array

Furthermore, we realized scalable fabrication of WS₂ nanodisk array with hundreds of nanodisks on the large CVD grown flakes (**Figs. 5.6** (a), (b)). The fluorescence image and zoom-in SEM image present the good periodic structure of our products, where the nanodisks are arranged close to each other with diameters of 300-400 nm. At selective locations as labeled 3-5 in **Figs. 5.6** (d), (f), unlike PL of the flake region nor that previously reported of CVD WS₂ [32], here A exciton peaks are well resolved. The PL images are constructed by extracting the integrated intensity of A exciton and defect bound exciton peaks, respectively (**Fig. 5.6** (c), (d)). Due to the limit of resolution of our system, the PL mapping of A exciton could only partially show the features of sub- μ m disks locating in majority of the patterned area. Though, the following fine line scan and single spectra analysis provide convincing evidences that we are able to produce regulated narrow, sharp and strong luminescence in large amounts. As for the mapping of defect emission intensity, distinct from the previous reported native emitters yielding very limited number of bright spots randomly distributed over the monolayers [33], we obtain the PL with the sharp defect peak emission in a large, two-dimensional region. As schematically shown in **Fig. 5.7** (a), within one laser spot, the disks are densely placed with gap and diameter which are smaller than the spatial resolution of our system. Thus, the mapping

image displays plane-like feature. The representative PL spectra corresponding to the labeled regions are presented in **Fig. 5.6** (d), which display strong sub-nm linewidth peaks of closed wavelengths. The blueshift of PL spectrum at room temperature (**Fig. 5.6** (e)) verifies the existence of strain in nanodisks which drives the PL evolution at low temperature. To investigate the wavelength control of sharp defect emission in our disk array, we conducted statistical analysis and found that 84% of sub-nm peaks are located within 608 to 616 nm, which is much narrower than the wavelength distribution of the previous artificial TMD emitter arrays [157,158,165].

We further examine the zoom-in PL mapping corresponding to number 1 bright spot in **Fig. 5.6** (d), which persist identical PL feature across the area in μm scale. In **Fig. 5.7** the patterned region corresponding to label 1 area have been examined by delicate PL mapping with step of 200 nm. **Fig. 5.7** (b) displays the mapping plot of spatially resolved PL intensity, at the integration range from 612 to 620 nm. The series of single spectra along the marked lines are presented in **Figs. 5.7** (c)-(e). These spectra predominantly express single sharp peak with small wavelength variations. The static data indicates that 85% of sub-nm peaks are located within 615-618 nm range. This results from properly positioned nanodisks with distance similar to their own diameters.

Compared to the previous TMD emitters, this method truly utilizes the large area of entire 2D plane rather than relying on the accidental occurrence of atomic defect or separately placed perturbations on substrate. This strategy paves the way for effectively producing quantum light source with large light emitting area in future.

Figure 5.6 (a) Optical image of WS₂ nanodisk array and flake, the scale bar is 50 μm. (b) Fluorescence image of WS₂ nanodisk array, scale bar is 15 μm. Inset is SEM image of disk array with scale bar of 1 μm. PL intensity mapping of WS₂ nanodisk array integrated from (c) 582 to 594 nm and (d) 608 to 620 nm at 4.2 K. (e) PL spectra of WS₂ flake and nanodisk array at room temperature. (f) Representative PL spectra corresponding to labeled regions in the PL mapping. (g) Distribution of the sub-nm peak emission wavelengths collected from different sites of the array.

Figure 5.7 (a) Schematic image of the mechanism of 2D emitter behavior. (b) PL mapping of region 1 in Fig. 5.6 (d), integrated from 612 to 620 nm. (c), (d), (e) The series of PL spectra taken along three marked lines with a step size of 400 nm. Statistics of the sub-nm peak emission wavelengths (f) and linewidths (g) correspond to the spectra taken from line 1,2,3.

Figure 5.8 PL spectra of WS₂ disk array taken at (a) 276 μ W and (b) 4 μ W excitation.

5.3.4 Confining the bound exciton in WSe₂

Last we discovered this lateral confinement is effective in other TMDs like WSe₂. As shown in **Fig. 5.9** (a), the WSe₂ nanodisks with various sizes were fabricated based on mechanically exfoliated flake. The diameter distribution is from 350 nm to μ m scale. The fluorescence image identifies the monolayer region with bright luminescence. In the sense of size dependent PL, it is depicted that the PL spectra of WSe₂ flake contains multiple narrow emission lines at 4.2 K (25 nW excitation). The large nanodisk (μ m scale) illustrates broad defect emission as well as multiple narrow peaks. In contrast, as the size is scaled down to 350 nm, the scattered narrow peaks and broad defect band transform into isolated emitter-like peak which is similar to the previously reported artificial WSe₂ emitters [157,158], but with much better spectral regulation towards single mode emission (**Fig. 5.9** (b)). Note that unlike the WS₂ nanodisks which maintain the sharp narrow peak emission at higher excitation power (**Fig. 5.8**), the WSe₂ nanodisks exhibits different power dependence with much smaller threshold power (**Fig. 5.9** (c)). At higher excitation powers (8.12 μ W), the PL spectra of small nanodisks display broad defect emission without isolated narrow peaks. When the power is reduced to nW scale, the isolated narrow peak emerges. This power dependence is possibly attributed to filling of defect

trapping states at higher excitations, which reduces the trapping potential for excitons [166]. Generally, the bound defect exciton emission will saturate with increasing power and yields a sub-unity power dependence after saturation point, which is in sharp contrast with A exciton [33]. Due to the various properties of defects the saturation power varies greatly case by case. These observations indicate a general strategy of achieving size tunable defect PL emission of TMDs.

Figure 5.9 (a) Optical image of WSe₂ nanodisk and flake. Inset is the corresponding PL mapping integrated from 700 to 770 nm, the corresponding scale bar is 4 μm. (b) PL spectra of WSe₂ nanodisks with different diameters at 4.2 K at 25 nW excitation. (c) PL spectra of small disk with different excitation power.

Remarkably, as the edge states and strain gradient are proposed to be the key to stimulate such isolation of narrow peaks, we found not only circular shape nanodisks but other extreme geometries with sharp corner and reduced dimensions are able to induce similar PL evolution on exfoliated WSe₂ (**Fig. 5.10**). The detailed shape driven isolation of emitter peaks is expected to be investigated in future, as it was also proposed in early studies of artificial emitters based on underlying nanostructures [158]. Beyond nanodisks, other TMD nanopatterns like

nanoribbons or nanoflowers with same fabrication process are also expected to tailor the defect emission, towards a unified defect engineering strategy based on as-prepared TMD samples.

Figure 5.10 (a) PL mapping of WSe₂ nanopattern integrated from 700 to 760 nm. The scale bar is 2 μ m. (b) Optical image of WSe₂ nanodisks with highlight of area with extreme geometry, which corresponds to the mapping area in (a), the scale bar is 3 μ m. (c) PL spectra taken from labeled positions in (a) at 4.2 K.

5.4 Conclusions

In conclusion, in this study we demonstrated an effective strategy to isolate the narrow defect emissions at 4.2 K by fabricating 2D semiconductor nanodisks. The controlled PL emission display emitter-like peaks with small wavelength variation, which is spectrally better confined than previously reported TMD emitters. The essential disk sizes to introduce PL confinement are obtained, which make it possible for the scalable fabrication of nanodisk array with high-yield narrow sharp emission with precise wavelength control in large scale. Moreover, this approach is very general and proved effective to WSe₂ as well. In addition to apparent benefits

to future quantum light source with controllable spatial and spectral positioning, this work also provides clean spectra features for optical probing of single defect which entangles with unique phonon mode [167] and single spin-valley state of localized individual carriers [168].

Chapter 6 Conclusions and prospects

6.1 Conclusions

In this thesis, extrinsic light emission of 2D semiconductors have been studied mainly by PL spectroscopy. Our contributions to the 2D research community are concluded mainly in three regards (**Chapter 3-5**). In the first part we demonstrate tunable excitonic emission of WS₂ upon DNA nucleobase coating, indicating a new type of optical sensing strategy. In the following part we depict a practical strategy to enhance valley polarization degree of trion by in-situ optical and electrical gating at 80 K and explain the results with theory of carrier screening effect on intervalley scattering. In the third part we found a deterministic isolation of narrow defect bound exciton in 2D semiconductor nanodisks.

Part I: tunable excitonic emission of monolayer WS₂ by DNA nucleobases

In this work, the WS₂-nucleobase interaction is systematically studied. We performed PL spectroscopy measurements on CVD-grown monolayer WS₂ on a SiO₂/Si substrate both before and after coating with DNA nucleobase, i.e., adenine, guanine, cytosine, and thymine solutions. We observed the conspicuous and distinguishable evolution of the excitonic states of the monolayer WS₂ upon the physisorption of adenine and guanine, whereas cytosine and thymine show a negligible influence, indicating the potential of CVD monolayer WS₂ for optically sensing DNA nucleobases. To reveal the sensing mechanism for DNA nucleobases and the doping of monolayer WS₂, the evolution of the PL profiles and the electrical transport features of monolayer-WS₂-based field effect transistors (FETs) were analyzed in detail. The results show that p-type doping is responsible for the optical effects. The typical doping level was further quantified by analyzing distinctive features in the PL spectra of monolayer WS₂ with various dopant concentration and calculated electron concentrations. These findings indicate the potential use of monolayer WS₂ for the optical detection of DNA nucleobases.

Part II: engineering polarization degree of monolayer WS₂ by physical doping

Inspired by a recent theoretical study together with an experimentally proved framework based on carrier screening effects on excitonic valley relaxation in 2D semiconductors [129,132], here we designed a strategy to greatly enhance P_c at liquid nitrogen temperature. Doping dependent circularly polarized PL spectra of monolayer WS₂ at temperature of 80 K under off-resonance excitation (2.33 eV) are studied. The carrier density of the sample is controlled by electrostatic and optical doping. The evolution of neutral and charged exciton emission states have been extracted. Surprisingly the electrostatic doping drives continuous increase of P_c for charged exciton emission. Besides, by controlling photoexcitation strength, a modulation of polarization degree is also depicted, parallel with the electrical doping effects. By comparing these findings with a general doping dependent valley relaxation mechanism and previous reports on exciton dynamics, we reveal the correlation between P_c and physical doping. Our results demonstrate the tunable valley polarization degree under low cost and Helium-free condition, equally effective as conducted under 10 T magnetic field [144]. We successfully enriched the understanding of valley relaxation process by electrostatic and optical doping means, which denotes an essential step towards practical valleytronic applications.

Part III: Deterministic Isolation of Bound Exciton Luminescence in 2D semiconductor Nanodisks

In this work we intentionally fabricated nanodisks based on monolayer WS₂ grown on SiO₂/Si substrate. The localized strain could lead to the formation of a potential well, which confines the defect bound exciton towards regulated PL emission. The size dependent PL evolution is clearly evidenced from broad defect band emission to isolated sub-nm peaks. This approach is proved reproducible with small spectral deviation within nanodisks of the same designed diameters. Based on the size control of defect PL, scalable production of such regulated emission is further realized by building nanodisk array, which demonstrates zero-dimensional quantum dot emission behaviour in two dimensions. Last we discovered that our approach is

also able to confine the PL emission in WSe₂, which indicates a universal strategy to control the defect bound exciton emission in TMDs towards next generation quantum communication architecture with precise site and wavelength positioning.

6.2 Prospects

(1) Dark exciton based molecular sensor

In **chapter 3** we introduced a nucleobase sensing strategy based on the charge transfer induced evolution of exciton/trion emission. Though for monolayer WS₂ the trion peak in PL spectra can be well resolved by Lorentz fitting, new sensing strategies still need to be explored in regards of new sensor concepts which are applicable to a broad temperature and energy range, combined with clear optical fingerprint upon molecule anchoring. Recently a conceptually new strategy has been theoretically proposed, based on brightening the dark excitons in tungsten based TMDs [169]. The preliminary theoretical results point out clearly that physisorption of molecules with a strong dipole moment can turn the dark K- Γ exciton bright resulting in an additional peak in optical spectra, which is well separated from A exciton (**Fig. 6.1**). In addition to sensing application, this prediction also shed light to brightening the dark exciton without magnetic field [35], towards enhanced light emission efficiency. Moreover, by tailoring the intervalley exciton dipole, valley polarization/coherence of both intra- and intervalley exciton could be considerably modified, providing another valley index for optical sensing.

We are going to experimentally prove this concept using WS₂ with photoactive molecules with a strong dipole moment like merocyanine, by PL and reflectance spectra at 80 K. We are going to change the concentration of merocyanine solution, which will increase/reduce the interaction among merocyanine molecules and in turn tailors the anchoring angle and corresponding exciton molecule coupling.

Figure 6.1 Excitonic dispersion and appearance of dark excitons. (a) Schematic image of electronic dispersion of TMDs. The bright K - K transition, dark K - Γ transition and exciton molecule coupling are labeled. (b) Excitonic dispersion with bright (dark) excitons exhibiting a center-of-mass momentum $Q = 0$ ($Q \neq 0$). (c) Calculated excitonic absorption spectrum of pristine and merocyanine-functionalized WS₂ on a silicon dioxide substrate at 77 K. Adapted from Ref. [169].

(2) Exploring the novel defect bound exciton properties based on nanopatterns with other geometries

In **chapter 5** it is found that not only nanodisks, but other extreme geometries are able to induce similar PL evolution. The exact shape dependence in regards of controlling defect bound exciton emission is still unexplored. Other nanopatterns like nanobelt, nanoribbons and nanoflowers are proposed to tailor the defect bound exciton as well.

Moreover, we observed novel linear polarization of defect exciton peak. Such linear polarization is in sharp contrast with previous report on defect emission of monolayer TMD

flakes [118], and consistent with the polarization dependence of colloidal monolayer TMD quantum dots [170], indicating a successful defect engineering and polarization confinement for our nanodisks. The potential mechanism behind this could be the creation of certain type of defect states or localized exciton entangling with strain modified phonons, which may inherit the polarization properties (angular momentum) from phonon [167]. Interestingly, such strain modified localized exciton emission is also tunable by extreme shape or dimensions discussed above. This additional degree of freedom may interact with intrinsic valley polarization and coherence of TMDs, providing a unique playground based on shape and size control of our nanopatterns [167,171].

Experimentally we are going to fabricate the nanopatterns as proposed, then measure angle-dependent Raman spectra of these samples. Based on previous reports [52] the angle dependence Raman could reflect the anisotropic strain and phonon confinement effect due to reduced lateral dimensions (**Fig. 6.2**). Then we will conduct linear/circular polarization resolved PL on nanopatterns at cryogenic temperature to study the polarization properties of narrow bound exciton emission. If the PL polarization is consistent with Raman, then it is very likely that such regulated narrow defect emissions are indeed coupled with novel phonon modes, which provides unique features of exciton-phonon coupling in TMDs with lateral confinement.

Figure 6.2 Polarized Raman spectra of the MoS₂ nanoribbon. (a) Raman spectra in the E' and A₁' peak regions of the 15 nm nanoribbons with respect to the polarization angle of the incident laser beam. (b) Schematic image for the polarized Raman measurement, the half-wave plate is used for both incident and scattered light. The polarization angle θ is with respect to the direction of the nanoribbons. (c) Polar plot of the experimental θ -dependent intensity of the E' and A₁' mode.

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