Manipulation of light-emitting properties of 2D materials by photonic nanostructures

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Declaration

This thesis is an account of research undertaken in the Nonlinear Physics Centre within the Research School of Physics and Engineering at the Australian National University between September 2014 and September 2017 while I was enrolled for the Doctor of Philosophy degree.

The research has been conducted under the supervision of Prof. Dragomir N. Neshev, Dr. Isabelle Philippa Staude, Dr. Manuel Decker, Dr Alexander S. Solntsev and Prof. Yuri S. Kivshar. However, unless specifically stated otherwise, the material presented within this thesis is my own original work.

None of the work presented here has ever been submitted for any degree at this or any other institution of learning.

Haitao Chen

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Publication

Journal Publications

Papers with results included in this thesis


Papers with results not included in this thesis


Selected Conference Presentations


Acknowledgments

When I firstly started to write the Acknowledgments part, I followed the same procedures as I did for other parts: reading the published thesis first and then trying to following the mature format. However, I felt something not right after writing down "Firstly I would like to thank...", I was running out of words, I felt these sentences were so "dry" and was far from enough to express my appreciation and gratitude, how can a precious more than 3-year-long time be squeezed into one or two pages? Of course, I know that there is nothing wrong to write in this way, it seems I do not even have better way to do it, so I finished the first version following the format listing all the people I would like to express my thanks for. However, I still felt somewhere not right.

Until one day, I read an article discussing the difference of expressing gratitude between eastern and western culture. It says, "In Chinese traditions, when you say 'please' or 'thank you', you are basically erecting a barrier between you and whomever you are speaking to. For the Chinese, politeness or such keqi (standing on ceremony) is associated with formality. As such, when you say thank to a friend what you are actually saying to them is that there is some need for formality between us...". Suddenly, it seems that I found the origin of my uncomfortable feeling. Having been brought up in a very traditional Chinese family, I still did not fully get used to use thanks naturally especially for deep gratitude though I have been in Australian for more than 4 years. In the bottom of my heart, I already treat my supervisors, colleagues, friends, families, who are always supportive, as the people I do not need any formality. I suddenly realized that this is likely the core reason why I felt something not right when writing the first version of the Acknowledgments. It is abstract and difficult to discuss the culture influence in detail here, I want to give out one short story how the people around support my phd.

During the second year of my phd, I spent quite a few months on some project starting from purchasing equipments and building up the measurement setup. We continued with experimental measurements taking lots of data. I was so excited when we observed expected phenomena after months’ hard work, we took more data and even organized a few discussion sessions with relevant people awaiting prominent results from this project. However, we found something unusual one day. What’s worse, after careful verification of the results, it turned out that the observed phenomena was artificial effect from one item we borrowed from another department. What a disaster for a phd student. I was so depressed feeling that I could not finish my phd...

Then, Dragomir, the chair of supervisor panel, came immediately after his trip back from Europe and told me "Do not worry, take some break, we are learning anyway..." with his usual encouraging smile.
One of my lab colleagues, Tingge Gao, helped with verifying the data again and again, told me similar story when he was a phd student trying to release my anxiousness.

My friends organized a trip to the beach after knowing my situation trying to cheer me up from the depression.

My girlfriend, Ran Gao, who is now my wife, always told me "I trust you, I believe that you could do better ", even though she has little understanding about my project.

Phd life is meaningful but not always easy, it has ups and downs. While I know that I could always count on the support from supervisors, collaborators, colleagues, friends and families without the need of any formality, which makes my phd life meaningful and colorful. At the end, I want to take the western manner saying thanks to all the people that support and accompany me during my phd, meanwhile, I will hold the deep gratitude in the bottom of my heart as the traditional culture imposes on me.

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Abstract

The development of two-dimensional (2D) materials brings up new opportunities for 2D physics and new applications. Among them, semiconductor transition metal dichalcogenides (TMDCs) show quite advanced properties. Especially, in the monolayer limit they become direct-bandgap semiconductors. The monolayer form demonstrates a range of optical effects including photoluminescence (PL), valley polarization and second-harmonic generation (SHG), which are important for future optoelectronic applications. However, the light-emitting efficiency of such monolayer TMDCs is generally low due to the subnanometer light-matter interaction length and defects. To enable their practical applications, new schemes are desirable to enhance the emission efficiency and further control properties such as directionality and polarization.

On the other hand, photonic nanostructures show great capability to manipulate light-matter interaction at the nanoscale. Thus, in this thesis, we explore different schemes to enhance and control emission from monolayer TMDCs by integrating them with resonant photonic nanostructures, including plasmonic structures, waveguides and nanoantennas. We have successfully demonstrated integration of monolayer TMDCs into different photonic platforms experimentally and showed great capability to control the emission from them. Associated theoretical work has also been presented. Our work shows potential important applications for future optoelectronic devices.

In Chapter 1, we firstly introduce the necessary background of the development of 2D materials and semiconductor optics. Then, we focus on the optoelectronic properties of 2D TMDCs. The prospect of integration of 2D materials with photonic nanostructures is further discussed.

In Chapter 2, we show integration of a monolayer MoSe$_2$ onto resonant plasmonic nanoantenna. Comprehensive control of the PL emission from quenching to enhancement is demonstrated by changing the thickness of the spacer between the MoSe$_2$ and nanoantenna. Further simulation results explain the experimental observation well.

In Chapter 3, we demonstrate enhanced and directional PL emission from WSe$_2$ monolayer integrated onto a silicon photonics structure. This is achieved by coupling the WSe$_2$ into a multi-resonant grating-waveguide structure which supports several leaky waveguide modes. Further theoretical work explains our experimental results well.

In Chapter 4, we propose a plasmonic-TMDCs scheme that could effectively separate the PL emission from different valleys of 2D TMDCs into opposite directions spatially. This is realized by simultaneously exciting both electric dipole and quadrupole modes from two-bar plasmonic antenna, the interference of radiation of these modes induces the spin-locked directionality.

In Chapter 5, we demonstrate enhanced SHG from a monolayer MoSe$_2$. This is achieved by integrating the monolayer onto a waveguide and exciting the material through evanescent field of the guided modes. The enhancement
is due to the fact that the waveguide geometry dramatically increases the nonlinear interaction length and allows for phase matching. Theoretical calculation further reveals the conversion mechanism in our system and points out further directions.

In Chapter 6, we summarize the work and discuss the future prospects in regards to the integration of 2D materials with resonant photonic nanostructures.
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Introduction

1.1 Thesis statement

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have many extraordinary electronic, mechanical, optical and chemical properties, and show great potential to be used in a wide range of applications. In particular, the monolayer form of 2D TMDCs crosses over to become direct-bandgap semiconductor and shows strong excitonic effects when interacting with light. This opens the door to many optoelectronic applications including atomic-scale single-photon emitter, transistors, novel light-emitting diodes and so on. However, the light emission efficiency of monolayer TMDCs is much lower than expected for direct-bandgap semiconductors, which is mainly due to the fact that the light-matter interaction length is limited by the subnanometer thickness, thus prohibiting them from many practical applications. Novel methods of enhancing the light-emitting efficiency and improving other emission properties are required.

Photonic nanostructures such as plasmonic structures, waveguides and nanoantennas are capable of controlling light-matter interaction at nanoscale and show great flexibility. Thus, the integration of a monolayer TMDCs with photonic nanostructures is promising to tune the light-emitting properties of these 2D materials. Such integration schemes have shown the capability of controlling the emission from a monolayer TMDCs, for example, ultralow threshold lasing from monolayer MoS$_2$ has been demonstrated by coupling to photonic crystal cavity. However, there is far more to explore in this direction in order to further enhance and control light emission from 2D TMDCs.

This thesis aims to develop novel photonic platform to enhance the light emission from monolayer TMDCs, and further control the other emission properties such as polarization and directionality. In general, photonic structures could be categorized into metallic and dielectric structures. They both have their own advantages. We explore both regimes of integration of TMDCs with metallic and dielectric structures based on request for linear and non-linear applications.
Following this logic, a brief introduction to discovery of 2D material and some fundamentals of semiconductor optics are given at the beginning of Section 1.2, then we move to overview of properties of 2D TMDCs. In Section 1.3, we focus on discussing the light-emitting properties of 2D TMDCs including photoluminescence (PL), single-photon emission, valley polarization and second-harmonic generation (SHG). At the end of this part, we also discuss the challenges facing 2D TMDCs for photonic applications. Following this, Section 1.4 firstly introduce the theoretical frame of enhancing spontaneous emission rate by Purcell effect, and then show the bright prosperity of integration of 2D TMDCs with photonic nanostructures, which also justifies our choice of the thesis topic. Section 1.5 presents motivation and outline of the thesis.

1.2 Overview of two-dimensional (2D) materials

‘What could we do with layered structures with just the right layers?’ Richard Feynman raised up this question in his famous lecture, ‘There’s plenty of room at the bottom’, in 1959. Among these ‘right’ layers, strict 2D materials at atomic scale are particularly interesting and have attracted lots of attention. Seeking for the real 2D materials in practice had been a long haunting dream.

1.2.1 Discovery of 2D materials

Although having been studied for long time as a theoretical model [1–6], 2D crystal of atomic thickness such as graphene was predicted to not exist, as they were thought thermodynamically unstable [7, 8] and was described as pure ‘academic’ material. However, people’s minds changed in 2004 when free-standing graphene was unexpectedly found in the lab [9], and particularly when the following experiments [10, 11] showed that the charge carriers inside graphene were indeed massless Dirac fermions. Figures 1.1(a) and (b) show the crystal structure of graphene and the first atomic force microscope (AFM) image of the graphene sample, respectively. The discovery of graphene not only brought Andre Geim and Konstantin Novoselov the 2010 Nobel prize in physics, it also opened the door to a gorgeous world of 2D materials.

When thinned down to a atomic layer, graphene shows quite different and distinguished characteristics compared to graphite, it even got a nickname of ‘miracle material’ due to its superior properties. From the perspective view of fundamental physics, the charge carriers inside graphene could be described as massless Dirac fermions, namely, the conduction electrons at low energies in graphene have a light-like linear dispersion and behave like massless. The electronic spectrum of graphene is shown in Fig. 1.1(c), which provides scientists with abundance of new physics [20, 21]. In terms of applied science,
Figure 1.1: Superior properties of graphene (a) The crystal structure of graphene: carbon atoms arranged in a honeycomb lattice [12]. (b) AFM image of the first exfoliated single-layer graphene showing its atomic thickness [9]. (c) Electronic spectrum of graphene inferred from experimental results in agreement with theory. This is the spectrum of a zero-gap 2D semiconductor that describes massless Dirac fermions with $1/300$ the speed of light [13]. (d) Transmittance spectrum of single-layer graphene (open circles) compared with theoretic prediction for two-dimensional Dirac fermions (red and green). The inset shows the transmittance of white light as a function of the number of graphene layers (squares). The dashed lines correspond to an intensity reduction by $\pi a$ with each added layer [14]. (e) Measured histogram of elastic stiffness from graphene showing high strength [15]. (f) Observed shift in G peak spectral position of Raman spectrum from graphene as a function of the change in total dissipated power, indicating superior thermal conductivity [16]. (g) Measured response of longitudinal conductivity to back-gated voltage from graphene encapsulated in hexagonal boron-nitride (solid lines) at different temperature, the dashed lines are theoretical calculation, where we could infer the high carrier mobility from graphene [17]. (h) Demonstration of extremely high current density sustained by graphene [18]. (i) Scatter plot of the gas leak rates dependence on the thickness of graphene layers measured from a graphene-sealed microchamber, indicating that atomic-scale graphene membrane is impermeable to standard gases including helium [19].
the amazing characteristics graphene owns rise up new opportunities for a wide range of applications. These includes but not are not limited to optical absorption of exactly $\alpha = 2.3\%$ ($\alpha$ is the fine structure constant) [Fig. 1.1(d)], super-high intrinsic strength [Fig. 1.1(e)], ultrahigh thermal conductivity [Fig. 1.1(f)], amazing room-temperature electron mobility [Fig. 1.1(g)], capability to sustain extremely high densities of electric current [Fig. 1.1(h)] and complete impermeability to any gases [Fig. 1.1(i)]. Graphene has shown its potential to be used in various areas, such as flexible electronics, photonics, energy generation and storage, sensors and metrology, bioapplications, paints and coating and so on [20–22]. It is almost impossible to name out all the potential applications and new physical phenomena graphene has brought to us. This atomically thin material has been an obsession for researchers around the world since its birth in the lab and new things are still coming out every day.

On the other hand, the message we could take from graphene is that the 2D materials have extraordinary properties compared to their bulk forms and hold huge potential for lots of applications, which is not fully explored at all. This inspired people to start looking for other graphene-like materials, such as boron nitride, transition metal dichalcogenides (TMDCs), black phorsphore, silicene and germanene. In particular, TMDCs are semiconductors and have shown many superior properties for applications in photonics. In this thesis, we will focus on TMDCs. To better serve for our topics, we start reviewing some basic concepts in semiconductor optics in the following section.

1.2.2 Introduction to semiconductor optics

The core of electronic technology is to control the flow of electrons, and photonics is the technology to control the flow of photons. Semiconductor optoelectronics connect these two technologies: photons create mobile charge carriers, and charge carriers in turn control the flow of photons. Semiconductor-based optoelectronic devices such as laser, light-emitting diodes have changed our life a lot and this field is still moving on quickly. Thus, studying optical properties of semiconductors, which is in the domain of semiconductor optics, is essential for fabricating advanced optoelectronic devices.

1.2.2.1 Electron, hole and exciton

Semiconductor is a crystalline or amorphous solid with electrical conductivity between conductor and insulator, typical examples include Si and GaAs. The conductivity of semiconductors could be altered by changing the temperature, doping with carriers or illumination with light. Atoms consisting of solid-state semiconductor could not be treated as single entity like hydrogen atoms, because they interact strongly with other nearby atoms. Thus, the conduction electrons in semiconductor are not bound to single atom, they
collectively belong to all atoms as a whole. In addition, atoms in lattice structure apply periodic potential on the electrons, the solutions to the Schrödinger equations for the electron energy form energy bands. In each band, a great deal of discrete energy levels are densely packed together, which could be well approximated as continuum. The concept of energy bands is illustrated in Fig. 1.2, the conduction and valence band are separated by a bandgap energy $E_g$. The bandgap energy is an important parameter when describing the electronic and optical properties of materials, and the value depends on material. For example, the $E_g$ is 1.2 and 1.42 eV (electron volts) for Si and GaAs at room temperature, respectively. The origin of the bandgap could be elucidated by Kronig-Penney model [23].

![Energy bands in semiconductor](image)

The electrons in the semiconductor obey the Pauli exclusion principle, this principle says that two or more electrons could not occupy the same quantum state and electrons fill up the lowest available energy level first. At absolute zero temperature, the valence band is fully occupied while the conduction band is empty, thus material is not conductive at all. However, with increasing temperature, some electrons will be thermally excited to transit from valence band onto conduction band leaving behind some unoccupied quantum states called holes. The electrons in the conduction bands act as mobile carriers and the unoccupied states in valence band allow other electrons to exchange places with applied electric field. Thus, the holes left in the valence band could be regarded as carriers with positive charge. The overall effect is that every electron excitation creates mobile carriers in both conduction and valence bands, free electron and hole, respectively. The concept of electron transition is illustrated in Fig. 1.2. The conductivity of semiconductor materials increases sharply with temperature as more and more charge carriers are generated.

Under certain excitation condition such as light illumination, exciton might be formed. Exciton is a bound electron-hole pair, the electron and hole interact with each other through Coulomb forces, similar to hydrogen atoms.
There are two basic types of excitons, free excitons and tightly bound excitons. The free excitons have large radius and are delocalized states, thus they can move freely throughout crystal. In contrast, tightly bound excitons have small radius and are bound to specific atom or molecule. Excitons can only exist in stable form when their attractive potential is large enough to protect them from collisions with phonons, the energy of these bound states is called binding energy. Excitons play an important role in determining the electronic and optical properties of semiconductors, especially for low-dimensional ones [24]. Other hybrid particle such as trion (bound states of two electrons and one hole, or one electron and two holes) or biexciton (bound states of two exciton) might be formed as well in some semiconductor systems.

Fermi level

At temperature $T$ under thermal equilibrium, the law of statistical mechanics says that the probability of a quantum state with energy $E$ is occupied, is given by the Fermi function

$$f(E) = \frac{1}{\exp[(E - E_f)/KT] + 1}$$ (1.1)

where $K$ is Boltzmann’s constant, and $E_f$ is a constant called Fermi energy or Fermi level. As can be observed from Eq. (1.1) $f(E_f) = \frac{1}{2}$, which means that the probability for electrons to take quantum states with energy of $E_f$ is $\frac{1}{2}$. The Fermi level is an important parameter when describing the electronic structure of semiconductor.

Effective mass

Energy-momentum relation ($E - k$) plays an essential role in accordance with wave mechanics. In free space, the energy $E$ and momentum $p$ relation for electron with mass $m_0$ ($9.1 \times 10^{-31}$ kg) could be obtained by solving the one dimensional time-independent Schrödinger equation, the solution is shown in Eq. (1.2). We could see from the equation that the $E - k$ relation is simply in a form of parabola.

$$E = \frac{p^2}{2m_0} = \frac{\hbar^2 k^2}{2m_0}$$ (1.2)

where $\hbar$ is the planck constant, $p$ is the magnitude of the momentum, $k$ is the magnitude of the wavevector $k=p/\hbar$.

In semiconductor, the motion of electrons is also governed by the Schrödinger
equation, but with a periodic potential created by charges in the crystal lattice structure as discussed. This effect results in not only separated energy bands, but also different Energy-momentum relations. The $E - k$ relations for both conduction and valence bands in Si and GaAs are shown in Fig.1.3. In addition, since the crystal structure is not always isotropic, the energy of electrons depends on both the magnitude and direction of the momentum. Fig.1.3 only shows the $E - k$ diagram for two specific directions.

Though the energy-momentum relation for electrons is quite different from free ones, while we could still observe from Fig.1.3 that the $E - k$ relation could be approximated by parabola at the bottom of the conduction band. The approximated relation is in the form

$$E = E_c + \frac{\hbar^2 k^2}{2m_c}$$ (1.3)

where $E_c$ is the minimum energy in the conduction band and $k$ is measured from the lowest point.

Compared Eq.1.4 and Eq.1.2 we could see that the behavior of electrons in the conduction band and the free electron is similar, but with a different mass ($m_c$). The $m_c$ is known as electron (conduction-band) effective mass. Thus, the effects that the lattices of ions apply on the motion of electron are incorporated into the effective mass, which is also the physical meaning of this quantity.

In the same manner, the $E - k$ diagram near the top of the valence band could be approximated as

$$E = E_v - \frac{\hbar^2 k^2}{2m_v}.$$ (1.4)
where $E_v = E_c - E_g$ represents the maximum energy in the valence band, $m_v$ is the effective mass of hole (valence band). Similarly, the $m_v$ accounts for the influence of the ion lattice on the valence-band holes.

The effective mass depends on both the crystal structure of material and the momentum direction, because the inter-atomic interaction in a crystal is orientation dependent. In addition, the effective mass varies with the band taken into consideration. Actually, there are usually a few parabolas coexisting at the top of the valence band depending on the types of holes.

### Spin-orbit coupling

In an atom, electron’s spin interacts with the magnetic field generated by its orbital movement around the nucleus, which is a typical example of spin-orbit coupling or interaction. This spin-orbit interaction results in shifting of the electron’s energy levels, the detectable signatures are the splitting of the spectral lines from atoms. Similarly, in solid semiconductor, electron’s spin momentum interacts with its orbital angular momentum, which results in a splitting of the energy bands. In solids, the spin-orbit coupling also relates to the dimension and symmetry of the materials [25]. In 2D materials, spin-orbit coupling plays a significant role [26].

#### 1.2.2.2 Direct and indirect bandgap

Based on the band structure, semiconductor materials could be categorized into two groups: direct- and indirect-bandgap materials. Direct-bandgap materials refer to semiconductors that have the same wavenumber $k$ (momentum) for the conduction-band minimum and the valence-band maximum energy. Materials that do not satisfy this condition are indirect bandgap. As observed from Fig. 1.3, GaAs has indirect bandgap while Si does not. Owning a direct bandgap or not makes a significant difference for semiconductors, especially when used as emitters. This is because electron transition from the conduction to valence band in indirect-bandgap materials must involve substantial momentum change of electrons, which requires much more efforts compared to direct-bandgap ones. For example, GaAs is good light emitter, while Si is not.

#### 1.2.2.3 Carrier recombination and photoluminescence (PL)

PL is the light emitted by a system following the absorption of photons. In a semiconductor, different mechanisms could lead to absorption and emission of light. The main ones are listed below.
• Interband transition. An absorbed photon could enable electrons to trans-
mit from the valence band to conduction band, creating an electron-hole
pair. The combination of electrons and holes will be accommodated with
photon emission.
• Impurity-to-band transition. This process usually happens in doped ma-
terials. Absorption of photon could enable transition between a dopant
and bands. The recombination process might be accompanied with ra-
diative photon emission.
• Excitonic transition. The absorption of photon could enable the for-
ma tion of exciton. The recombination of the electron and hole might result
in photon emission, called exciton annihilation. Recombination of hy-
brid particles such as trion and biexciton might be involved in radiative
emission too.

The above processes might also involve nonradiative processes, for exam-
ple, interband transition might be assisted by one or a few phonons. There
are also other nonradiative processes such as intra-band transition (transition
inside bands) and phonon transition. The internal quantum efficiency $\eta_i$ for
photon emission of a semiconductor material is defined as the ratio between
the radiative electron-hole recombination rate and total recombination rate.
The internal quantum efficiency is an important parameter to describe the
light emission efficiency of a material. Usually, it is expressed in the form

$$\eta_i = \frac{r_r}{r} = \frac{r_r}{r_r + r_{nr}}. \quad (1.5)$$

where $r = r_r + r_{nr}$ is the total recombination rate, $r_r$ and $r_{nr}$ are the radiative
and nonradiative recombination rate, respectively.

So far, we have introduced some fundamental concepts in semiconductor
optics including bandgap, exciton, internal quantum efficiency and so on. In
the following section, we will focus on discussing the optical and electronic
properties of 2D TMDCs, where these concepts will appear often.

1.2.3 2D transition metal dichalcogenides (TMDCs)

1.2.3.1 Basic composition and structure

TMDCs refer to a group of materials with the formula MX$_2$, where M is a
transition metal element from group IV (Zr, Ti, Hf and so on), group V (such
as V, Nb or Ta) or group VI (Mo, W and so on) in the periodic table, and X is
a chalcogen (S, Se or Te). These materials possess many interesting electronic,
mechanical, optical, chemical and thermal properties and have been studied
by researchers for a long time [27–29]. Figure 1.4(a) shows a picture of the
bulk form of MoS$_2$, one example of TMDCs, which has been used as dry
lubricant and catalysis. Generally, these materials have layered structures of the form $X$–$M$–$X$, a plane of metal atoms sandwiched by the chalcogen atoms in two hexagonal planes, as shown in Fig. 1.4(b). Adjacent layers are held together weakly by van-der-Waals forces to form the bulk crystal in various polytypes, which are different in stacking orders and metal atom coordination, as shown in Fig. 1.4(c). The overall symmetry of TMDCs is hexagonal or rhombohedral, and the metal atoms have octahedral or trigonal prismatic coordination [30].

Inspired by graphene, the monolayer of TMDCs could also be formed by micromechanical cleavage from bulk crystal, Figure 1.4(d) shows the first reported microscopic image of the monolayer MoS$_2$ prepared by cleavage. Figure 1.4(e) shows the atomic force microscopic image of the sample shown in Fig. 1.4(d). Figure 1.4(f) shows the cross-sectional plot along the red line in Fig. 1.4(e), which shows that the monolayer thickness of TMDCs is around 0.65 nm. Despite that the bulk form of TMDCs has been studied for a long time, the same material shows quite distinguished and advanced properties when thinned down to atomically thick layer, especially in a monolayer form. In particular, semiconducting TMDCs (MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$ and so on) show great potential for photonic applications. In the further section, we will discuss in more details the properties of 2D TMDCs.

1.2.3.2 Electronic structure

The 2D versions of TMDCs offer properties that are complementary to yet distinct from those in graphene. Graphene by nature is semi-metallic without a bandgap and only trivial bandgap ($<0.25$ eV) could be obtained from engineering [34], which does not fit with digital electronics and greatly limits its applications where semiconductors are needed. In contrast, 2D TMDCs such as MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$ are semiconductors and have bandgaps of amplitudes comparable to conventional group III–V ones [35, 36]. Especially, in the monolayer form, TMDCs such as MoS$_2$ cross over to become direct bandgap (indirect bandgap in bulk) with gaps located at the K and K’ points [35, 37] of the electronic spectrum. This is a result of an increased indirect-gap size due to the substantial quantum confinement effect in the out-of-plane direction, while the direct gaps at the K and K’ points remain almost unaffected [7, 38, 39]. Figure 1.4(g) shows the band structure of bulk and monolayer MoS$_2$ calculated from first-principles density functional theory (DFT) [33]. In particular, 2D material are promising to scale the transistors in digital electronics to ever-smaller dimensions considering their atomic thickness and the lack of short-channel effects [40]. Semiconductor 2D TMDCs are suitable as channel materials in field-effect transistors, as they are structurally stable and have carrier mobilities comparable to Si [41, 42]. Figure 1.4(h) shows the schematic image of the first top-gated transistor based on a monolayer MoS$_2$, which showed excellent on/off current ratio (~$10^8$), room temperature mobility of over 200 cm$^2$ V$^{-1}$ S$^{-1}$ and subthreshold swing of 74 mW per
1.2 Overview of two-dimensional (2D) materials

Figure 1.4: Basic properties of 2D TMDCs. (a) Image of bulk MoS$_2$ about 1 cm long [30]. (b) Schematic of the three-dimensional image of a typical MX$_2$ structure, in which the yellow atoms represent for chalcogen (X) and the grey ones as metal atoms (M) [31]. (c) Schematic representation of MX$_2$ polytypes of different structures: 2H (hexagonal symmetry), 3R (rhombohedral symmetry) and 1T (tetragonal symmetry). The yellow atoms are chalcogen (X) and the grey atoms are the metal (M). The lattice constants are in the range of 3.1 to 3.7 Å depending on materials [32]. (d) Optical image of the first single-layer MoS$_2$ obtained by micromechanical cleavage [31]. (e,f) Atomic force microscopic image of a single layer of MoS$_2$ on a SiO$_2$/Si substrate (e), and the cross-sectional plot along the red line (f) [31]. (g) Band structures of bulk and monolayer MoS$_2$ calculated from first-principles density functional theory. The horizontal dashed line represents the Fermi level [33]. (h) Schematic structures of the first transistor built based on a monolayer MoS$_2$ [31].
decade \cite{31}. In contrast, graphene-based transistors could not achieve high on/off ratio due to the lack of bandgap.

The electronic structure of monolayer TMDCs can be modeled through an effective 2D massive Dirac Hamiltonian with the spin and valley pseudospin (K or K') degree of freedom, where valley pseudospin refers to degenerate energy extrema in momentum space \cite{26, 43}. As shown in Fig. 1.4(b), the monolayer TMDCs have out-of-plane mirror symmetry, while no in-plane inversion symmetry \cite{26}. Besides, spin-orbit coupling is strong in 2D TMDCs arising from the d orbitals of the heavy metal atoms \cite{44}. The strong spin-orbit coupling, together with the inversion symmetry breaking, bring lots of valley-contrasting optical \cite{26, 45–49} and electronic \cite{26, 50, 51} properties in 2D TMDCs, thus a wide range of related applications. The valley-selective light emission from 2D TMDCs will be discussed later. In addition, the electrical transport properties in monolayer TMDCs are also valley-dependent \cite{50}, for example, the valley Hall Effect (in analogy to the spin Hall Effect) has been demonstrated in monolayer MoS$_2$ \cite{52}.

Table 1.1: Electronic properties of selected 2D TMDCs \cite{36}.

<table>
<thead>
<tr>
<th></th>
<th>MoS$_2$</th>
<th>MoSe$_2$</th>
<th>WS$_2$</th>
<th>WSe$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective masses (in $m_0$) \cite{26}</td>
<td>~0.5</td>
<td>~0.6</td>
<td>~0.4</td>
<td>~0.4</td>
</tr>
<tr>
<td>Optical gap $E_g$(eV) \cite{26, 37, 53}</td>
<td>~2</td>
<td>35</td>
<td>53</td>
<td>1.7</td>
</tr>
<tr>
<td>Exciton binding energy (eV) \cite{59} or 0.9 \cite{60} (Th.) or 0.2 or 0.4 \cite{61} (Exp.)</td>
<td>~0.5</td>
<td>59</td>
<td>or 0.5</td>
<td>62 (Th.)</td>
</tr>
<tr>
<td>Conduction band spin–orbit splitting (meV) \cite{63}</td>
<td>~3</td>
<td>~20</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>Valence band spin–orbit splitting (meV) \cite{26, 63}</td>
<td>~150</td>
<td>~180</td>
<td>~430</td>
<td>~470</td>
</tr>
</tbody>
</table>

Th. and Exp. represent theoretical and experimental results, respectively. $m_0$ is the electron mass.

Besides, 2D TMDCs have multiple polymorphs in crystalline structures, including 1H or 1T for monolayer and 1T, 2H and 3R for a few layers, as indicated in Fig. 1.4(c). This variation in their structure and composition enables broad tunability in functionalities. Table 1.1 \cite{36} lists the basic electronic properties of the group-VI TMDCs, where we see that the variation in composition provides characteristics in a broad range, while graphene does not have flexibility in this respect.

1.2.3.3 Optical properties and optoelectronic applications

The electronic structure of 2D TMDCs discussed above directly influences their optical properties. Compared to conventional semiconductor materials, the exciton binding energy of a monolayer TMDCs is around one order of
magnitude larger, as predicted by theory [59, 60, 64–66] and verified by experiments [55–58]. The large exciton binding energy induces strong excitonic effects in these materials. For example, the optical absorption spectrum shows sharp resonant features [35, 37], which is consequence of the dominating direct transitions between the valance and conduction band states around the K and K’ points [26, 43]. The strong excitonic effects cause a significant transfer of oscillator strengths from the band-to-band transition to the 1s exciton state [67]. The ratio of the oscillator strength of the 1s to the band-to-band transitions is up to 100 [36, 68, 69]. This large exciton oscillator strength induces strong light-matter interaction for these 2D TMDCs. Absorbance as high as 0.1–0.3 have been reported for a monolayer of MoS₂ [35, 53]. Besides, the strong excitonic effects also lead to short 1s radiative lifetime, which is inversely proportional to the oscillator strength [68, 69].

Furthermore, higher-order excitonic quasiparticles such as trion [53, 54] and bi-exciton [70, 71] have also been observed in 2D TMDCs. Interestingly, these quasiparticles also have much larger (roughly an order) binding energy than those in conventional quasi-2D semiconductors [53, 54, 70–72], which makes them observable even at room temperature. These might bring many possible applications such as creation of high-temperature and high-density coherent quantum states of excitons [73].

In addition, excitons trapped at anisotropic potentials from spatially localized defects in 2D TMDCs give rise to single-photon emission [74–77], which is indispensable for quantum optics and photonic quantum technologies [78]. More details will be given in Sec. 1.3.1.

Consequently, the exceptional electronic and optical properties of 2D TMDCs give rise to exciting new physics, as well as opening the door to many novel optoelectronic applications. 2D TMDCs-based photodetectors working via the mechanism of photoconduction [35, 52, 79, 83, 85, 86] and photocurrent [80, 81, 87–92], structure of in-plane [80, 87–89, 91, 92] and out-of-plane junctions [81, 83, 90, 93], have all been demonstrated experimentally. These 2D TMDCs photodetectors mostly operate on the basis of photovoltaic effect and have lower dark current, compared to graphene-based ones. Responsivity as high as 880 A W⁻¹ has been reported [79]. A schematic photograph of one of such devices is shown in Fig. 1.5(a). Energy-harvesting device based on a monolayer of WSe₂ with power conversion efficiency comparable to a conventional bulk one has also been demonstrated [80]. The relation between the photocurrent and the bias voltage under different conditions are shown in Fig. 1.5(b). What is more, heterostructure consisting of different kinds of 2D TMDCs with gate-tunable photovoltaic response have shown great potential for optoelectronic applications. One example of the device structures is shown in Fig. 1.5(c) [81]. In addition, devices based on graphene-TMDCs junctions also offer great opportunities for various optoelectronic applications [82, 83, 94, 95]. Photoreponsene down to a few ps has been demonstrated from a monolayer graphene /WSe₂/graphene device [82, as shown in Fig. 1.5(d). External quantum
Figure 1.5: 2D TMDCs-based photodetectors and modulators. (a) Schematic of a monolayer MoS$_2$-based photoconductor showing high sensitivity. The top image shows the photocurrent mapping of the device, where we could observe a hotspot at the location of the monolayer MoS$_2$ [79]. (b) Photocurrent dependence on the bias voltage for a monolayer WSe$_2$ device with split gate electrodes (top inset) under various bias conditions. Solid green/blue lines, p-n/n-p; dashed green/blue lines, n-n/p-p. The electrical power $P_{el}$ from the device could be extracted when working as a diode. The low inset shows the relation between $P_{el}$ and the bias voltage [80]. (c) Schematic representation of a MoS$_2$/WSe$_2$ heterojunction device with lateral metal contacts, showing gate-tunable photovoltaic response. The top inset shows the enlarged crystal structure [81]. (d) Time-resolved photocurrent from graphene/WSe$_2$/graphene heterostructure photodetector for different thickness of WSe$_2$. The response time for monolayer device extracted here is around 5.5 ps [82]. (e) Photocurrent as a function of the bias voltage for a graphene/WSe$_2$/graphene device under laser illumination energy of 2.54 eV [83]. (f) Image of a TMDC-based saturable absorber modulated visible fiber laser [84].
efficiency as high as 50% has been observed from TMDC-graphene structures [83, 94]. Figure 1.5(e) shows the photocurrent dependence on the bias voltage for one of the examples. Besides, TMDCs-based saturable absorber modulated fiber laser in visible range has been demonstrated too [84, 96], one example is shown in Fig. 1.5(f). Considering the rich variation of the 2D materials, there is great potential to explore TMDCs-based heterostructures for applications.

In particular, the 2D confinement, strong excitonic effects, spin-valley coupling and inversion-symmetry breaking in 2D TMDCs give rise to many interesting light-emitting properties, such as PL, single-photon emission, SHG and so on. These light-emitting properties make 2D TMDCs potentially serve as versatile light sources, which is missing in graphene. In the following section, we will focus on discussing various light-emitting properties in 2D TMDCs.

1.3 Light-emitting properties of 2D TMDCs

1.3.1 PL properties

As discussed above, the monolayer TMDCs cross over to become direct bandgap semiconductors and show strong excitonic PL emission at the atomic level [35, 37]. Figure 1.6(a) shows the PL spectra from a monolayer and a bilayer MoS$_2$ at room temperature, where we could observe that the single layer exhibits PL orders of magnitude stronger than that of the bilayer. On the other hand, the wide range of bandgaps of the 2D TMDCs, as shown in Table 1.1, offer vast options of PL emission in the visible and near-infrared range. What’s more, the PL spectral position and intensity from 2D TMDCs could be tuned by strain [97][Fig. 1.6(b)], electrical gating [54][Fig. 1.6(c)], chemical doping [98][Fig. 1.6(d)], temperature [99][Fig. 1.6(e)], composition [100][Fig. 1.6(f)] and so on. In addition, the heterostructure consisting of different 2D TMDCs add more options for tunable PL emission [81, 101, 102]. The vast variety and broad tunability make 2D TMDCs ideal candidates for the light-emitting layers for flexible optoelectronics and other potential applications [30, 36].

On the other hand, due to the out-of-plane quantum confinement in the 2D TMDCs, isolated defects from them could serve as single-photon emitters. Four independent studies reported single photon emission from defects in them in the same period [74–77]. Figure 1.7(a) shows one example of the PL mapping of the quantum emitters from the monolayer. The emission linewidth of these quantum emitters is quite narrow (~0.1 meV), compared to the broad linewidth of the free exciton emission (~10 meV), as shown in Fig. 1.7(b). Photon antibunching features from time-correlation measurements show that these emitters are indeed single-photon emitters [Fig. 1.7(c)]. Interestingly, under finite magnetic field, the spectral wandering from the doublet...
Figure 1.6: Broad tunability of PL from 2D TMDCs. (a) PL from a monolayer MoS$_2$ compared to that from a bilayer. The inset shows how the PL intensity decreases with increasing number of layers [35]. (b) Absorption (left panel) and PL (right panel) spectrum of a monolayer MoS$_2$ under tensile strains up to 0.52% along the zigzag direction [97]. (c) PL from a monolayer MoSe$_2$ as a function of the back-gate voltage, the $X^0$ represents emission from neutral exciton, and the $X^+$ and $X^-$ are emission from positively and negatively charged excitons respectively [54]. (d) Tuning of PL from a monolayer MoS$_2$ by chemical doping. The inset shows the normalized spectra [98]. (e) Normalized PL spectra from a monolayer MoS$_2$ for different temperatures [99]. (f) PL emission from Mo$_{1-x}$W$_x$S$_2$ monolayer with different composition x. The peak refers to the emission from the A and B excitons [100].
Figure 1.7: Single-photon emission from 2D TMDCs. (a) PL mapping of isolated quantum emitters in a monolayer WSe$_2$ [75]. (b) Typical emission spectrum from the quantum emitters shown in panel (a), it shows much narrower linewidth (~0.1 meV, left inset) than that of free excitons (~10 meV, right inset) [75]. (c) Time-correlation measurements showing obvious photon antibunching confirms the single-photon nature of the emission shown in panel (b) [75]. (d) Energy splitting between the doublet from the quantum emitter as a function of the applied magnetic field [75]. (e) Voltage-dependent quantum emission from a monolayer WSe$_2$, X and Y represent two different emitters [76]. (f) Spectrally integrated voltage-dependent emission profiles from the line X and Y shown in panel (e), here a 5 meV window is used [76].
emission disappear and the extracted Zeeman splitting goes up with increasing field intensity, as shown in Fig. 1.7(d), this further confirms that the doublet emission is from the same single quantum emitter [74–77]. These emitters show advanced emission properties compared to those in self-assembled InGaAs quantum dots [103] and delocalized excitons [104]. Importantly, electrical control of the quantum emission has also been demonstrated [76], as shown in Fig. 1.7(e) and (f). In addition, cascaded single-photon emission has also been observed from monolayer WSe$_2$ [105], which paves the way for new quantum optical experiments in 2D materials. In particular, single-photon emission was also reported from oxidized WS$_2$ [106] at room temperature. Single-photon emitters with long lifetime and coherence time will play an essential role in photonic quantum computing [78,107]. The ‘flat’ quantum emitters from 2D TMDCs show great potential for such applications. Besides, the single-photon emitters embedded in the atomically thin TMDCs are expected to have better tunability and be more feasible to integrate with other electronic devices, compared to other solid-state single-photon emitters [36,108].

What’s more, light-emitting diodes (LED) based on 2D TMDCs have shown great potential to be used as excitonic emitters, which are based on electron-hole recombination. Different types of LEDs such as Schottky junctions [89], p-n junctions [87,90,91] and vertical tunnel junctions have all been demonstrated. Low threshold down to a few nanoamps [80] and external quantum efficiency up to 10% [93] make these TMDCs-based LEDs suitable for future optoelectronic applications such as chip-integrated emitters. Importantly, emission in these excitonic LEDs is tunable by controlling the injection bias [87,93], which makes them attractive for electrical integration. In contrast, the highest reported emission efficiency of graphene-based LED is only around 0.3%, which is based on thermal radiation of hot electrons [109]. In addition, the unique valley-dependent characteristics of 2D TMDCs provide these LEDs with controllable polarization, more about that will be discussed later.

1.3.2 Valley pseudospin

As discussed previously, the lack of an inversion center and strong spin-orbit coupling in the electronic structure of 2D TMDCs lead to unique valley-based physics and applications [36,43,112]. Figure 1.8(a) shows the trigonal prismatic structure of monolayer TMDCs (upper part), the honeycomb structure without center of inversion symmetry and the 2D first Brillouin zone (lower part) [36]. The energy-degenerate valleys K and K’ facilitate the valley degree of freedom and valley-based selection rules, as illustrated in Fig. 1.8(b). Furthermore, the spin-orbit coupling splits the spin degeneracy at each valley and locks the spin and valley pseudospin degrees of freedom: the spin-up state at the K valley and the spin-down state at K’ are degenerate [26,36,43], which is shown in Fig. 1.8(b) as well. Importantly, this valley degree of freedom is addressable by optical pumping: pumping with circularly polarized light of
Figure 1.8: Valley properties of 2D TMDCs. (a) Trigonal prismatic structure of monolayer TMDCs (upper part), the honeycomb lattice structure with broken inversion symmetry and the 2D first Brillouin zone with the high-symmetry points (lower parts) [36]. (b) Electronic bands near the K and K’ points, the spin (up and down arrows) and valley (K and K’) degree of freedom are locked together. $m$ is the azimuthal quantum number [36]. (c) Circular dichroism spectra from monolayer MoS$_2$ under circularly polarized light excitation, in which the opposite sign of circular luminescence is caused by the valley splitting [47]. (d) Electrical control of circularly polarized emission from WSe$_2$-based light-emitting transistor. The middle part illustrates the contribution to electroluminescence from two valleys. The lower part shows the circularly polarized electroluminescence for two opposite current directions, as schematically indicated in the top insets [110]. (e) The source-drain bias voltage dependence on the Hall voltage for the monolayer MoS$_2$-based transistor under right (red solid line), left (red dashed line) circularly polarized and linearly polarized (red dotted line) light modulation. The blue solid line shows the results of a bilayer device under right circularly polarized light modulation. These results are a signature of a photoinduced anomalous Hall effect (AHE) driven by a net valley polarization [52]. (f) Polarization-resolved SHG measurements for left ($\sigma^+$) and right ($\sigma^-$) circular components under $\sigma^+$ excitation [111].
different handedness could populate electrons into a specific valley \cite{46,47}. Figure 1.8(c) shows one example of how optical pumping could address the valleys and control the polarization of the PL emission \cite{47}. Vice versa, the valley-dependent optical properties also make it possible to fabricate TMDCs-based LEDs with controllable emission polarization \cite{87,91,110}. In these cases, the electric field at the p-n junctions preferentially pumps the carriers into one specific valley, depending on the biased field direction, thus the electric field could switch the dominant handedness of the emitted light by changing its direction, as shown in Fig. 1.8(d) \cite{110}. Such a TMDCs monolayer p-n junction could also be useful in light detection, Figure 1.8(d) shows a transverse valley-polarized current with the illuminated light of different polarization, which is called photoinduced anomalous Hall effect (AHE) \cite{52}. A light harvesting device based on valley polarization has also been demonstrated \cite{80,113}. In addition, the valley degree of freedom and the strong excitonic effects also induce exceptional selection rule in the nonlinear regime, namely, the emitted SHG is anti-circular polarized with respect to the excitation \cite{111,114}, as shown in Fig. 1.8(f). What is more, excitonic valley coherence \cite{49}, valley- and spin-polarized Landau levels \cite{115} and valley Zeeman effect \cite{116–119} have all been demonstrated in monolayer TMDCs too. Optical \cite{120,121}, magnetic \cite{104,122} and electrical \cite{49} control of the valley pseudospin in 2D TMDCs have also been developed lately. The dynamic control of valley index opens up extraordinary opportunities for valleytronics: devices based on control of the electrons’ valley degree of freedom, which is potentially another dimension for carrier to encode information \cite{43}. Overall, the valley-spin coupling in 2D TMDCs bring both new valley-associated physical phenomena and novel applications \cite{26,112}, which requires more exploration. As mentioned, the spin-valley coupling also has impacts on the nonlinear properties of the 2D TMDCs, we will discuss more nonlinear characteristics of 2D TMDCs in the following section.

1.3.3 Nonlinear optical properties of 2D TMDCs

The nonlinear optical properties of materials have been applied in wide range of applications and are important parts for modern optics \cite{123}. 2D TMDCs also show exceptional nonlinear responses including SHG \cite{124–126}, sum-frequency generation \cite{127}, four-wave mixing \cite{127} and third harmonic generation \cite{128,129}. In particular, SHG from 2D TMDCs due to their symmetry breaking has attracted a lot of attention, because the ultrathin layer shows strong SHG considering their atomic thickness \cite{124}. The SHG possesses some extraordinary properties, such as broad tunability \cite{58,114}. Importantly, the ultrathin nature and passive surface of 2D TMDCs make them suitable for integration with silicon photonics platforms \cite{130,131}, which is promising for enabling second-order nonlinearity in the silicon photonics platform, as silicon itself does not have such property due to symmetry structure. More details of SHG from 2D TMDCs will be discussed below.
SHG from 2D TMDCs

Figure 1.9: SHG characteristics from 2D TMDCs (a) Power dependence of SHG from a monolayer MoS$_2$, the upper inset shows the fundamental spectra (red) and the SHG (blue). The lower inset shows the layer-dependent intensity of the SHG [125]. (b) The intensity of the parallel (blue squares) and perpendicular (black circles) polarization components of the SHG from monolayer MoS$_2$ as a function of the angle between the laboratory and MoS$_2$ crystalline coordinates [125]. (c) SHG from a monolayer WSe$_2$ as a function of 2x energy of the pumping, which reveals the resonant behavior of the SHG [58]. (d) SHG intensity from monolayer WSe$_2$ in resonance with the exciton at selected gated voltage [114]. (e) SHG mapping as an effective tool to determine the different grain boundaries of a CVD-grown monolayer MoS$_2$ [132]. (f) SHG mapping used to determine the polytypes of MoS$_2$ ultrathin layers [133].
As discussed above, the lack of inversion symmetry in monolayer TMDCs not only gives rise to exceptional electronic and optical properties, it also allows strong optical SHG, which does not exist in its bulk form due to symmetry [123]. On the other hand, nonlinear optical responses are an important aspect of light-matter interaction and play an essential role in various photonic and optoelectronic applications. 2D TMDCs might offer great potential both in the linear and nonlinear regime, considering their superior mechanical, electronic and optical properties, as well as flexibility for integration [36, 112, 130]. Intense SHG have been demonstrated from different materials such as MoS$_2$ [124, 125, 134], MoSe$_2$ [135], WS$_2$ [136]. Figure 1.9(a) shows one example, the SHG from monolayer MoS$_2$ and its dependence on the power and layer number [125]. The parallel and perpendicular components of the SHG (refer to the excitation laser polarization) show a six-fold pattern as a function of the angle between the laboratory and the MoS$_2$ armchair axis, as shown in Fig. 1.9(b). This pattern reflects the 3-fold-rotational symmetry of the crystal structure [125, 134]. Interestingly, the SHG intensity from monolayer TMDCs could be tuned by the pumping wavelength dynamically (resonant or non-resonant to the exciton transition) [58] [Fig. 1.9(c)] and electric gating [114] [Fig. 1.9(d)]. This tunability might enable new approaches to optical signal processing. What’s more, nonlinear optical imaging has been shown as an all-optical way to determine the crystal orientation of 2D TMDCs at a large scale [132] and bring a reliable tool to probe the structure features of 2D TMDCs [133], as shown in Fig. 1.9(e) and (f), respectively. All these nonlinear features of 2D TMDCs show great potential for future photonic applications.

1.3.4 Challenges facing 2D TMDCs for photonic applications

Though 2D TMDCs possess extraordinary optoelectronic properties and show great potential for applications in photonics, such as light-emitting device, a number of challenges still remain. Firstly, the PL quantum yield from monolayer TMDCs measured so far is much lower than the expected value for a direct-gap semiconductor. For example, the value reported from monolayer MoS$_2$ is only around 0.004 [35]. Secondly, the atomic thickness of such 2D TMDCs restricts their interaction length with light, which limits some applications and the efficiency. Besides this, controlled large-scale growth is also one of the main challenges, but it is beyond the scope of this thesis.

To address the challenge of the limited emission efficiency in 2D TMDCs especially in monolayer form, in this thesis, we develop the solutions to integrate 2D TMDCs with photonic nanostructures to boost their emission efficiency and further control other properties. The reason we choose this method is due to that various photonic nanostructure including plasmonics [137], waveguides [131], nanoantennas [138, 139] and photonic cavities [140] could effectively manipulate light-matter interaction at nanoscale with great flexibility. Indeed, integration of 2D TMDCs with photonic nanostructures has
shown great potential for enhancing the performance of 2D TMDCs and is also crucial for future photonic circuit applications \[30, 36, 112\]. In the following section, we will firstly discuss the general principle of integration 2D TMDCs with photonic nanostructures, then some examples of integration of 2D TMDCs with photonic nanostructures will be given to illustrate the bright prospect of this method.

### 1.4 Integration of TMDCs with photonic nanostructures

#### 1.4.1 Purcell effect and emission enhancement

The spontaneous emission rate of an emitter not only depends on the inherent properties of the materials, but also on the electromagnetic environment it interacts with, which is well known as the Purcell effect. Thus, we could modify the emission rate through changing the environment. Purcell made the first proposal to put atom inside cavities to enhance its magnetic transition in 1946 [141].

To describe the modification of the emission rate, we use the quantified term Purcell factor. It is defined as the ratio between the modified and the free-space emission rate. For an emitter whose transition frequency aligns with the cavity resonance and has a narrower linewidth compared to the resonance width, when the emitter locates at the maximum field in the cavity mode and the dipole moment aligns with the polarization of cavity mode, the Purcell factor $F_p$ is [142–144]

$$F_p = \frac{\Gamma_g}{\Gamma_0} = \frac{3Q\lambda^3}{4\pi^2V_0} \quad (1.6)$$

where $\Gamma_g$ and $\Gamma_0$ are the emission rate in the cavity and free space, respectively. $\lambda$ is the wavelength of transition, $Q$ is the quality factor of the cavity, $V_0$ is the volume of the cavity mode. This equation tells that we need resonators that could confine light into small volume and keep it for a long time to modify the emission rate significantly. However, the two requirements for resonators seems contradictory since better confinement usually accompanies with higher loss. The research of modification of spontaneous emission is mostly about developing better trade-off between these two aspects [144].

Metal nanoparticles and photonic crystal cavities are the two most commonly used resonators to enhance the emission from emitters. In metal nanoparticles, the light field could be confined beyond the diffraction limit through coupling to electron oscillation, or plasmons, in metals. With the development of nanofabrication techniques, nanoparticles of different geometries and smaller size have been designed to achieve better confinement of
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Figure 1.10: Examples of photonic resonators. Schematic designs of plasmonic nanoparticles of different geometries: bar (a), cube (b) and bowtie (c). Photonic crystal cavities working on modes of different types: planar (d), vertical (e) and optomechanical (f). The colored dots refer to modes confined by these resonators.

light. Figure 1.10 shows a few examples of these designs, such as bar (a), cube (b) and bowtie (c). With plasmonic metal nanoparticles, the optical field could be confined in the scale of down to 10 nm, and even smaller mode volume could be obtained by confining light in the gaps between nanoparticles [145]. However, the cost we need to pay for such strong confinement is the high damping loss from metals. The quality factor of the plasmonic metal nanoparticles is in the order of ten [146]. In contrast, photonic crystal cavity could achieve quality factors as high as millions [140]. But photonic crystal cavity works on the principle that light is confined due to reflections enabled by the periodic dielectric structures. Thus the mode volume of these cavities is limited by the diffraction limit, which is around $0.1(\lambda_0/n)^3$. Here $\lambda_0$ is the free-space wavelength, and $n$ is the refractive index of the medium. Various photonics crystal cavities have been developed to perform improved enhancement of emission. Figure 1.10 also shows a few examples of these designed on planar (d), vertical (e) and optomechanical (f) modes. In addition, we could also use photonic structures to concentrate or increase the absorption of the excitation light to enhance the emission from emitters, so photonic structures with multiple resonances could be applied to boost both the excitation and emission processes to achieve best overall light harvesting.

What is more, by coupling to different types of modes excited in the plasmonic nanoparticles or dielectric cavities, other radiation properties of emitters, such as directionality and polarization, could be well controlled too. Thus, integration of emitter with photonic nanostructures is a promising way to control the emission properties of emitters and further enable practical optoelectronic applications.
1.4.2 Control of light emission from TMDCs through photonic integration

Figure 1.11: Coupling of 2D TMDCs with photonic cavities. (a) Integration of a monolayer WSe$_2$ with a photonic crystal cavity. The WSe$_2$ exciton energy and the cavity resonance are aligned [147]. (b) Polarization-resolved spectra, taken from the device shown in panel (a), demonstrating the laser emission [147]. (c) Exciton-polariton dispersion in a monolayer MoS$_2$-microcavity system measured through angle-resolved reflection spectroscopy. The dashed red line shows the exciton energy, solid red lines trace the dispersion of the cavity polariton modes [148]. (d) Dispersion relation extracted from the measurements shown in panel (c). The red spheres and solid black lines are the polariton energy and their theoretical fits respectively, which shows a Rabi splitting of 46 meV [148]. (e) Micro-PL mapping of the monolayer MoS$_2$-nanocavity device. The region 3 corresponds to the defect area in the photonic crystal cavity, where we could observe obvious PL enhancement compared to other regions [149]. (f) The spectra taken from the 4 different regions, as shown in panel (e) [149].
Introduction

The atomically thick 2D TMDCs have naturally passivated surfaces without any dangling bonds, which makes them suitable to integrate with photonic structures, including planar photonic crystal cavities [147, 149, 150], optical microcavities [148, 151], optical ring resonators [152] and so on. Lasing with low threshold has been demonstrated by integrating 2D TMDCs with photonic cavities [147, 151], one example is shown in Fig. 1.11(a) and (b). Polaritons from strong coupling between 2D TMDCs and cavity modes have also been observed in different systems [148, 151], one of such observation is shown in Fig. 1.11(c) and (d). Besides, a photonic cavity could effectively enhance and shape the PL from 2D TMDCs [149, 150], Figures 1.11(e) and (f) show one example.

These cases listed above justify that light-matter interaction in 2D TMDCs could be effectively enhanced and controlled through integration with photonic nanostructures. However, there is a lot more to explore in this field, especially considering the great flexibility and potential offered by photonic structure. For example, what is the crucial factor that affects the light emission performance when integrating 2D TMDCs with various photonic structures such as plasmonics? How to extend the light-matter interaction length for 2D TMDCs through photonic integration? How to design the proper structure to manipulate the valley properties? In this thesis, we are exploring novel methods to control and manipulate light-emitting properties of 2D TMDCs by integration with photonic platforms.

1.5 Motivation and thesis outline

2D TMDCs show great potential for optoelectronic applications especially to be used for a future versatile tunable light source including novel LEDs, ‘flat’ emitters and low-power laser, as discussed in Section 1.3. However, the PL quantum yield of these materials are far lower than expected for direct-bandgap semiconductor and the atomic thickness intrinsically limits the light-matter interaction length, which prohibits them from realizing many practical functionalities. Integration with resonant photonic nanostructures is promising to enhance the emission from such 2D TMDCs and further engineer their emissive properties such as polarization and directionality, which are crucial for lots of practical applications. Though some work has been done about integration of 2D TMDCs with photonic structure, it is far from enough and there is still a lot to explore. In this thesis, we focus on developing novel photonic platforms to enhance and engineer the emission from monolayer TMDCs including plasmonic structures, waveguides and nanoantennas.

Localized plasmon resonances are known to be good for controlling light emission from nanoemitters due to high Purcell effect, thus could offer good means to manipulate emission from 2D TMDCs. In Chapter 2 we demonstrate the integration of monolayer MoSe₂ with a resonant plasmonic nanoan-
Motivation and thesis outline

Ten antenna array, and show full control of the PL from strong enhancement to quenching through changing the spacer thickness between the nanoantenna and the monolayer MoSe\textsubscript{2}. Our simulations further reveal the crucial factor that affects the PL performance of the plasmonic-monolayer-MoSe\textsubscript{2} system. When we published our work, this was the first demonstration of MoSe\textsubscript{2}-plasmonic integration and showed great control of the emission.

Though plasmonic structures could effectively manipulate the light emission from 2D TMDCs, the enhancement relays on local hot spot, hence it is crucial to control the distance between the plasmonic structure and the monolayer TMDCs precisely, if we want to harvest the emission, as learned from the experiments in Chapter 2. The distance is usually in nanometer scale and hard to implement in practice. Furthermore, the gold or silver plasmonic structures are not compatible with silicon platform widely used in modern photonics. To address this issue, in Chapter 3, we demonstrate a monolayer WSe\textsubscript{2}-loaded waveguide-grating system based on the silicon photonics platform. This Si-based system supports multiple resonances, originating from different modes supported by the waveguide. This enables us to combine the excitation and emission enhancement at the same time. What is more, this system could effectively guide the emission components of different polarization from WSe\textsubscript{2} into different directions, which is induced by the dispersion of the grating for different modes. The platform demonstrated here could be used for a chip-integrated multi-functional light source, as well as for applications such as visible light communication.

Valley polarization in 2D TMDCs inspires lots of new physical phenomena and shows great potential applications in valleytronics, such as information encoding. In Chapter 4, we propose a TMDCs-nanoantenna scheme that could effectively route emission from different valleys into opposite directions spatially. By mimicking emission from monolayer TMDCs as circular dipole emitters, we demonstrate numerically that a simple two-bar plasmonic nanoantenna could realize such functionalities. The directionality derives from the interference of the electric dipole and quadrupole modes excited in the nanoantenna. Thus, we could tune the emission direction of such TMDCs-nanoantenna system by just choosing to address different valleys (changing the polarization states of the pumping). Such TMDCs-nanoantenna shows great potential for applications like information encoding and processing.

Monolayer TMDCs possess intense SHG due to inversion symmetry breaking and show lots of potential applications in the nonlinear regime. Especially, they are suitable candidates for integrating with Si photonics platform without any lattice-mismatch issues (a problem for conventional III/V materials). Such integration could enable many second-order nonlinear functionalities in silicon photonics, because silicon itself does not have second-order nonlinearity due to the symmetric structure. However, the nonlinear interaction length of 2D TMDCs is limited by the subnanometer thickness, thus the overall nonlinear conversion efficiency is low. To overcome this issue,
in Chapter 5, we demonstrate integration of monolayer MoSe$_2$ onto silicon waveguide. By pumping the monolayer MoSe$_2$ through the guided modes, we achieve around 5 times enhancement of the SHG compared to excitation from free space. This enhancement is due to the fact that the waveguide configuration dramatically increases the nonlinear interaction length and allows for phase matching between the fundamental and second-harmonic fields. Furthermore, our theoretical calculations reveal how the internal mode conversion works and points out future directions to achieve better nonlinear performance. This work demonstrated here shows that the limited interaction length of 2D TMDCs could be effectively extended by waveguide integration, which opens door to many on-chip applications such as spontaneous parametric down conversion and parametric amplification.

In Chapter 6, we summarize the work that have been done and discuss about the possible future directions and outlook.
Manipulation of PL from 2D MoSe\textsubscript{2} by plasmonic nanoantenna

2.1 Introduction

As discussed in Chapter 1, 2D TMDCs have lots of advanced properties and show great potential for future optoelectronic applications \[30,36,43,112\]. Especially, in photonics, these atomic materials are promising to be used as versatile light-emitting source as presented in Section 1.3. However, the PL emission efficiency of such 2D materials is much lower than we expect for a direct gap materials \[35\], which limits many practical applications. On the other hand, novel integrated devices utilizing the properties of TMDCs have been demonstrated, including ultra-sensitive photodetectors \[79\] and low threshold lasers \[153\]. In the latter, the interaction between TMDC and a photonic crystal cavity emphasizes the importance to enhance the emission from such 2D semiconductors through interactions with photonic nanostructures.

Emission from quantum emitters could be well controlled by localized plasmon resonances (LPR) sustained by metallic particles due to high Purcell enhancement \[137,141\]. As such, the hybrid systems of plasmonic nanoparticles with 2D TMDC materials have been a subject of intense interest. By the time our work came out, research in hybrid systems composed of plasmonic nanostructures and TMDCs had mainly focused on MoS\textsubscript{2}. Effects such as photocurrent enhancement \[Fig. 2.1(a)\] \[154\], PL enhancement by plasmonic gold nanoantenna \[155\] and nanoshell structure \[156\] have been demonstrated\[Fig. 2.1 (b) and (c)\]. In the work shown in Fig. 2.1 (b), they demonstrated around 65\% PL enhancement and peak shift, which were attributed to the plasmonic enhanced optical absorption and subsequent heating of the MoS\textsubscript{2} monolayer \[155\]. In the work shown in Fig. 2.1 (c), the PL enhancement effect was also mainly due to the enhanced optical absorption \[156\]. Afterwards, plasmonic cavity coupled to both the excitation and emission was also designed to achieve better PL enhancement from monolayer MoS\textsubscript{2} \[157,160\]. Figure 2.1 (d) shows one example of the plasmonic cavity with double resonances \[157\]. Besides, plasmonic bowtie antenna with Fano resonance was
Manipulation of PL from 2D MoSe$_2$ by plasmonic nanoantenna

Figure 2.1: Control of monolayer MoS$_2$ properties by plasmonic. (a) Photocurrent enhancement induced by plasmonic gold nanoparticles from a monolayer MoS$_2$-based transistor [154]. (b) PL enhancement from a monolayer MoS$_2$ through integration with resonant plasmonic gold bars. Left: MoS$_2$-gold hybrid structure, right: 2D PL mapping of the system [155]. (c) Spectra of a monolayer MoS$_2$ with (green) and without (red) gold nanoshell deposition on top [156], the inset shows the scattering spectrum of the gold nanoshell. (d) Schematic image (left) and mode profiles (right) of double resonant plasmonic cavity designed to enhance the PL from a monolayer MoS$_2$ [157]. (e) Reflection spectrum from a bowtie plasmonic antenna-MoS$_2$ hybrid system showing Fano resonance [158]. (f) PL quenching effect from a gold-MoS$_2$ hybrid system [159].
also demonstrated to control the emission and reflection of monolayer MoS$_2$ [158] [Fig. 2.1 (e)]. What’s more, atomic-scale morphological detection [161], and nanophotonic circuit composed of a single silver nanowire and MoS$_2$ flake [162] have been studied too. Plasmonic enhancement of PL has also been explored in WS$_2$ monolayers (PL at shorter wavelengths of $\approx 620$ nm) by coupling to gold nanoparticles [163]. However, in a number of these experiments, the inter-band absorption peak of gold (500–600 nm) could likely have affected the enhancement effect. While there are other members in the TMDCs family with emission in the infrared range (away from gold enhanced inter-band absorption) remained unexplored, such as MoSe$_2$. Besides, most of these experiments demonstrated emission enhancement of TMDCs as a combination from excitation and emission processes. Compared with enhancement in the excitation process, enhancement in the emission is more robust as it does not depend on the pumping scheme, which is especially important for electronically pumped emitting devices. More thorough investigation is desired in this respect.

Interestingly, the inverse effect namely PL quenching, has also been reported when investigating a Au-MoS$_2$ hybrid system [159]. They attributed the quenching to the charge transfer from the monolayer MoS$_2$ to the gold nanoantennas through the resulting Schottky barrier of 0.4 eV. However, the quenching of PL emission from the monolayer should also happen at very small distances between the antennas and the TMDC due to the coupling of the emitted photons into non-radiative plasmonic resonances of the nanoantennas, i.e. dark plasmonic modes [164]. Nevertheless, the control of PL from 2D materials in the full range from PL quenching to enhancement by varying the coupling to the plasmonic antennas (through the variation of the spacing to the TMDC) remains so far not explored.

Here, we study the coupling between a monolayer MoSe$_2$ and gold nanoantenna arrays mainly focusing on emission process. PL manipulation from quenching to enhancement was realized by changing the thickness of a spacer used to spatially separate the 2D material and the antenna arrays. Numerical simulations support our observed phenomena and reveal the coupling mechanism in this hybrid system. MoSe$_2$ is used here because it has some superior properties compared with well studied MoS$_2$, though both are of similar structure. Firstly, MoSe$_2$ exhibits a smaller bandgap, higher electron mobilities, higher internal quantum efficiency, and much narrower line width compared to the extensively studied MoS$_2$ [165–167]. These intrinsic characteristics imply different applications compared to MoS$_2$. Secondly, few-layer MoSe$_2$ possesses a nearly degenerate indirect and direct bandgap, which makes it more suitable for external modulation of bandgap and optical properties [165]. Thirdly, the direct bandgap of MoSe$_2$ is close to the optimal bandgap value of single-junction solar cells and photoelectrochemical devices [167]. Importantly, MoSe$_2$ has a lower Fermi energy level (4.4 eV) [168], resulting in reduced charge transfer when in contact with gold. While MoSe$_2$ is an appealing candidate for coupling to gold plasmonic nanostructures with
PL in near-infrared range (away from gold’s enhanced dissipation due to inter-band transitions), this has remained unexplored to date.

2.2 Plasmonic nanoantenna design and sample fabrication

The emission of TMDCs could be generally altered by metal particles, such as these used in our experiments, in two ways. Namely, enhancing the local field in the excitation process or the local density of states in the emission process, at the location of the nanoemitter. Whereas the first effect directly translates to an increase of the excitation rate, the latter modifies the spontaneous emission rate. Such modification of the spontaneous emission rate is commonly referred to as the Purcell effect [141]. Generally, modification of the spontaneous emission rate is more robust way for controlling the emission of such TMDCs as it does not depend on the pumping scheme, which is especially important for emitting devices that are electronically pumped. However, placing a nanoemitter close to a metal particle also creates additional, non-radiative channels due to the dissipative nature of metals at optical frequencies. This basically happens when the emitter couples to the higher order plasmonic modes that are non-radiative in nature. When an emitter is located too close to the antenna, the non-radiative relaxation rates can dominate, spoiling the benefits of the radiative decay rate enhancement introduced by the plasmonic nanoantenna. This competing process in the weak pumping regime can be quantified by the quantum yield, defined as the ratio between the radiative and total decay rates. PL modification, the readily measurable quantity that is commonly used in experiments, thus relies on a combined consideration of the excitation rate enhancement and the quantum yield [164, 169–175]. The goal of our experiments is to investigate these processes especially regarding the emission part in a system composed of plasmonic gold-bar nanoantenna, and a monolayer of MoSe$_2$.

Figure 2.2: The key step-to-step fabrication procedures for gold plasmonic nanoantenna. The glass substrate is 100 μm and is cleaned by aceton and isopropanol before ITO coating. The dimensions are not to scale.
Figure 2.3: Photographs of the samples with/without spacer. (a and b) Schematic side view of the two samples, without spacer and with spacer respectively. (c and d) The corresponding SEM images of the two samples used in experiments. PL spectra of spots a in the region of MoSe$_2$-on-antenna and b in the region of MoSe$_2$-on-substrate are shown and compared in Fig. 2.4 (c) and (d). (e and f) Magnified SEM images of the area bounded by dashed rectangles in (c) and (d) accordingly showing the shape of the antenna and how the monolayer flakes are positioned on antennas. The antenna length for the sample without a spacer is 127 nm and 100 nm for the sample with a spacer.
Rectangular gold nanoantennas with fixed width and height, both of 40 nm, and varying lengths in the range 70 – 130 nm were prepared and arranged in a square lattice with a center to center distance between adjacent elements of 505 nm. The nanoantennas were fabricated by standard electron beam lithography (EBL). The key step-to-step fabrication procedures of these plasmonic nanoantenna is shown in Fig.2.2. In step 1, a 10 nm indium tin oxide (ITO) was coated by physical sputtering on the glass for conducting and adhesion purposes before we start our lithography process. In step 2, we spin coated PMMA495A4 resist with two consecutive produces, 500 revolutions per minute (rpm) for 5 seconds for photoresist spreading and 4000 rpm for 1.5 min for coating, both at acceleration of 1200 rpm/s. Then post baking is applied to the sample at 180 °C for 3 minutes, the resulting photoresist layer thickness is around 200 nm. In step 3, we perform EBL using Raith 150 (voltage of 20 kv and aperture of 7.5 µm). After electron-beam exposure, development is performed using cold 1:3 MIBK to IPA with a development time of 35 s, followed by a rinse in isopropanol for 30 s. After development, in step 4, thin layer of Titanium (around 3 nm) and gold (40 nm) are slowly deposited by Electron Beam Thermal Evaporation. In step 5, sample are immersed into hot acetone to remove the unwanted part to form the designed structures.

After characterizing the transmittance spectra of these samples, some samples are coated with a thin layer silica by physical sputtering. The layer thickness was measured by ellipsometry. Such an antenna was chosen because their two different localized surface plasmon can be selectively excited by using different optical polarizations. Next, single layer of MoSe\(_2\) samples were mechanically exfoliated from the bulk crystal and transferred onto the sample containing the plasmonic nanoantennas. The plasmon resonance of the antenna array is around the MoSe\(_2\) PL peak at \(\approx 785\) nm. At the same time, a second set of samples with slightly lower resonant wavelengths were coated with a thin layer silica spacer of 8.5 ± 1.5 nm through physical sputtering (the thickness is measured by an ellipsometer after the coating). The resonant wavelengths slightly red shifted due to the coverage, because of the increase of the surrounding refractive index as experienced by the localized surface plasmon polaritons. This sample was designed such that the plasmon resonance spectrally coincides again with the the MoSe\(_2\) PL peak after application of the spacer layer. Then another piece of exfoliated monolayer of MoSe\(_2\) was transferred onto the spacer-coated sample. For reference purposes, we let the monolayer flakes on both samples sit partly on the antenna array and partly on the silica substrate coated with a thin layer of indium tin oxide. The schematic pictures of our two samples are shown in Fig.2.3(a) and (b), respectively and the corresponding SEM images are given in Fig.2.3(c) and (d). Figure 2.3(e) and (f) show the gold nanoantennas and how the monolayer flake is positioned on the sample accordingly. The morphology of the TMDC on the nanoantennas was also tested by an AFM measurement in a non-contact mode, which reveals the conformal coating of the monolayer on top of the antennas.
Plasmonic nanoantenna design and sample fabrication

Figure 2.4: Spectra properties of the samples. (a) Transmittance profiles of the sample without spacer obtained by white light spectroscopy, the electric field of the illumination is polarized along the antenna long axis (solid blue line) and perpendicular to the long axis (dashed black line), respectively. (b) Transmittance profile of the sample with spacer before (blue line) and after coating the spacer layer (dashed red line), for illumination with its polarization along the antenna long axis. The transmittance for polarization perpendicular to the antenna’s long axis are identical in this spectral region before and after coating the spacer layer, as shown with dashed black line. (c) PL spectral profiles of the sample without spacer corresponding to points a (solid blue line) and b (dashed blue line) in Fig. 2.3(c), the legend ‘ant’ here means on antenna and ‘sub’ means on substrate (same in the following). (d) PL spectral profiles of the sample with spacer corresponding to points a (solid blue) and b (dashed blue) in Fig. 2.3(d). (e and f) Normalized spectra of c and d, respectively.
Figure 2.4(a) and (b) show the transmittance spectra of our antenna arrays with and without spacer obtained by polarized white light spectroscopy, respectively. Here we distinguish the polarization of the incident illumination by its electric field that is either perpendicular or parallel to the long axis of the plasmonic rectangular nanoantenna. The experimental setup used to measure the transmittance is shown in Fig. A.2. The spectra show pronounced transmittance dips near the central emission wavelength, marked with vertical dashed red line, when the polarization is set to be parallel to the long axis. Note that the contrast of the transmittance dips is not high due to the sparse arrangement of the antennas. Importantly, the antenna resonance disappears when changing the polarization of the incident illumination to be perpendicular to the antenna long axis (dashed black lines), confirming that the measured resonances are a consequence of the excitation of LPR in the nanoantennas.  

To make sure that the MoSe\textsubscript{2} flakes used for our samples are monolayers, we measure their PL spectra excited by a 532 nm continuous-wave laser. The PL results are shown in Fig. 2.4(c) and (d), which all show a good agreement with results for monolayer MoSe\textsubscript{2} reported previously [165, 176], thus confirming that the flakes we used in experiments are monolayers. Furthermore, we have also conducted Raman measurements on the flakes excited by the same laser wavelength. While less accurate than the PL identification, the measured first Raman peak of the flakes at 377 cm\textsuperscript{-1} is consistent with the results for monolayer MoSe\textsubscript{2} [165, 176]. Therefore, we could conclude that the MoSe\textsubscript{2} flakes we used in experiment are monolayers.

2.3 PL characterization

Next we investigate how the spectral profiles of the monolayer MoSe\textsubscript{2} are affected by the nanoantennas. Micro-PL spectroscopy and micro-PL spatial mapping was performed using a commercial WiTec alpha300S system in scanning confocal microscope configuration as shown in Fig. A.3. For excitation, light from a supercontinuum laser with 5 nm spectral bandwidth tunable in the range 530 – 640 nm is focused on the sample with a 100× objective (NA=0.9) from the MoSe\textsubscript{2} side. The measured spot size of the excitation beam is \( \sim 1 \mu m \) at 532 nm wavelength. The MoSe\textsubscript{2} PL is then collected from the substrate side of the sample using a 50× (NA=0.65) objective (transmission mode). A linear polarizer inserted into the detection path allows for selectively collecting the PL for different polarizations. In order to remove the light of the exciting laser source from the signal, a 715 – 1095 nm bandpass filter was introduced. The spectrometer is fiber-coupled to an Ocean Optics spectrometer using a multimode (non-polarization maintaining) fiber to neutralize any possible polarization sensitivity of the spectrometer. To further rule out any unwanted effects from possible gold PL, we have tested the PL from base gold antennas, which was found to be below the noise level of our detection. For spatial mapping, the MoSe\textsubscript{2} has been excited with an average power of 0.5 \( \mu W \), leading to an excitation power density of 637 W/cm\textsuperscript{2} on
Figure 2.5: **PL emission control by the plasmonic antennas.** (a and b) Optical images of two samples, without a spacer and with a spacer, respectively. (c and d) Corresponding typical PL mapping images of the samples integrated over the range 715 – 1095 nm, both images are normalized to their respective maximum value. (e and f) Corresponding antenna effects varying with collection polarization angles of the two samples, measured data (asterisks) and fitting curves (red solid lines). The insets in e and f indicate the direction of polarization with respect to the gold rectangular antenna.

The PL has been collected for different polarizations using an avalanche photodiode in combination with a long-pass filter.

The PL spectra of two typical regions, point a (in MoSe$_2$-on-antenna region) and point b (in MoSe$_2$-on-substrate region) [Fig. 2.3(c) and (d)], using excitation of 532 nm, are shown in Fig. 2.4(c) and (d), respectively. The measured PL from the monolayer MoSe$_2$ shows that the PL is quenched for the
Manipulation of PL from 2D MoSe$_2$ by plasmonic nanoantenna

Note that the absolute value of PL signal on MoSe$_2$-on-substrate region in Fig. 2.4(d) (sample with spacer) is lower than its counterpart in Fig. 2.4(c) (sample with no spacer). This is likely due to the variation of the sample quality and not due to the spacer material. As already mentioned, our monolayer MoSe$_2$ flakes were exfoliated from bulk crystal, hence the sample properties like size and formation may vary from one flake to another. As such, the PL signal could vary for different flakes. Besides, to obtain proper PL signal in experiments, we have further adjusted the excitation laser power accordingly for different samples. Thus, the comparison of the absolute PL values from different samples does not represent valuable information. Here we focus on the comparison of the PL on different parts of the same flake, which excludes variations of the PL signal from other factors like the sample quality. If the two samples we used in experiments were exactly the same, the PL value on MoSe$_2$-on-substrate region shown in Fig. 2.4 would be the same. The normalized spectra are also shown in Fig. 2.4(e) and (f) accordingly. The flake on the sample without spacer shows slightly red-shifted and broadened spectrum on the antenna compared with the PL spectra on the substrate. The origin of the quenching effect cannot be unambiguously identified here, however it is likely due to the ohmic losses \[^{164}\] as well as possible additional charge transfer effect \[^{159}\], as the flake is in direct contact with the antenna. The changes of spectral position and intensity are relatively small compared to MoS$_2$ \[^{159}\], suggesting that the charge transfer is not as strong as in MoS$_2$, which is supported by the larger Schottky barrier of 0.7 eV \[^{159,168}\]. Therefore, we believe that the dominant reason for quenching is the increased non-radiative decay of the emission from the MoSe$_2$ in close proximity to the gold antennas.

In contrast, the sample with a spacer shows almost the same spectral shape of emission for both MoSe$_2$-on-antenna and MoSe$_2$-on-substrate regions as shown in Fig. 2.4(f), which is different from the results of broadened and red-shifted spectra reported in the literature \[^{155,160}\] about MoS$_2$. This is a strong indication that the stronger PL on MoSe$_2$-on-antenna region is mainly caused by emission enhancement and implies increased radiative decay due to plasmonic coupling in our system. Otherwise ohmic effects brought by the excitation enhancement will broaden and shift the spectral profiles \[^{155}\]. Moreover, this unchanged spectra with enhanced intensity characteristic of this system is particularly beneficial for practical devices based on MoSe$_2$ when considering its stability, as well as some optical applications that require stationary spectrum such as interferometry.

To further understand the influence of the antenna on the PL, we map the 2D PL image integrated over the spectral region 715 – 1095 nm. The optical images of the two flakes are shown in Fig. 2.5(a) and (b), accordingly and the results of PL mapping are shown in Fig. 2.5(c) and (d) (both images are normalized to the corresponding intensity maximum), respectively. Both, the quenching effect for the sample without spacer and the enhancement for sample with spacer can be clearly seen there. We can also see that the emission
from the gold antenna or the substrate regions is negligible as compared to the region covered by the monolayer MoSe$_2$ flakes, which means the background is negligible.

In the following, we define the quantitative PL change due to coupling with antenna, called here antenna effect, as $\text{PL}_\text{ant}/\text{PL}_\text{sub}$. This quantity is calculated by taking the average PL value of a small area from the MoSe$_2$-on-antenna region then subtracting the corresponding background and normalizing to the PL from the same area at MoSe$_2$-on-substrate region, namely $(1 - 2) / (3 - 4)$, as shown in Fig. 2.5(c) and (d). It can be seen from the definition that the antenna effect would be greater than 1 for PL enhancement while less than 1 for quenching. We also collect the PL at different polarizations by adding a polarizer in the collection pathway and obtain the antenna effect varying with polarization angles, as shown in Fig. 2.5(e) and (f) for both samples, respectively. We observe approximately threefold maximal enhancement of the PL from the MoSe$_2$ monolayer for the sample with a spacer, while nearly up to fourfold quenching for the sample with no spacer. The antenna effects are obviously polarization dependent for both samples due to the excitation of the dominant LPR along the long antenna axis. We note that in our measurements we cannot clearly distinguish the individual antenna spatially, hence our measurements represent the average quantity of enhancement across the entire unit cell of the antenna array. This averaging reduces the effective enhancement/quenching effect, which can be much greater for some positions of the emitters (see the Numerical Modeling section below). Besides, the strongest enhancement effect happens when the polarization is along the antenna’s long axis, which reflects the intrinsic property of LPR resonance along the long axis.

To investigate the interaction mechanisms of these hybrid systems in more detail, we measured the antenna effect variations with respect to different pumping wavelengths using a supercontinuum laser tunable in the range of 530-640 nm. No significant dependence was found in the PL emission by varying the excitation wavelength by more than 100 nm. This excitation wavelength insensitivity implies further that the observed phenomena are mainly induced by interaction between the antenna and MoSe$_2$ during emission process, and the excitation does not affect our measurements much. This behavior is confirmed in our numerical modeling part below.

2.4 Numerical modeling

To support our experimental results and further understand the nature of the involved processes, we perform numerical calculations. The numerical calculations also allow us to see the effects of fine variation of the spacer thickness, which is not possible in our experiments due to the percolation of the dielectric spacer on top of the antenna for small thicknesses ($< 6$ nm).
Figure 2.6: Schematic representation of the simulation. (a) Schematic of the model structure. On the left we show a dipole emitter (red arrow) above a metallic nanoantenna where the distance has been controlled with a spacer. On the right we show the reference situation that is geometrically the same except the antenna is missing. (b) XZ cross section of the simulation setup, \(d\) indicates the spacer thickness, the coordinates are consistent with the one shown in (a). (c) The enhancement of the electric field by the antenna, normalized to the reference case, calculated in a XY plane 7 nm above the antenna. The antenna (top view) is excited by a plane wave of the wavelength \(\lambda = 532\,\text{nm}\), polarized parallel to its short axis. The strongest field enhancement appears at the edges of the antenna.

Finite Element Method (FEM) solver, as implemented in the commercially available software package COMSOL, were used to perform the numerical calculations. The simulations were performed with open boundary conditions. To analyze the emission properties, an electric dipole emitter is placed in the computational domain and its emitted field has been calculated everywhere in space. The radiative decay rate was calculated by integrating the outward, normal component of the normalized Poynting vector through a surface surrounding the antenna and the dipole emitter. The total decay rate took the non-radiative losses into account, which are calculated by integrating the Ohmic losses across the volume of the antenna. Both energies require a normalization to the energy emitted by the same source into the same background material.

The antenna considered here has both width and thickness of 40 nm and a length of 127 nm. The length was tuned to be resonant at the emission wavelength of \(\lambda = 785\,\text{nm}\). To avoid nonphysically sharp edges, we model the antenna as rounded with a radius of curvature of 10 nm. The considered gold properties are based on experimental data from [177] for the permittivity of gold in the visible/near-infrared spectral region. The thickness of the ITO is set to 10 nm and its refractive index is taken from [178]. The glass substrate (SiO\(_2\)) is modeled as a half-space and has a constant refractive index of \(n = 1.44\). To avoid numerical artifacts, a minimum distance of 2 nm between the dipole emitter and the ITO or the antenna, respectively, is introduced.
To analyze the emission process, the interaction of an electric dipole emitter and the antenna is considered in the weak coupling regime. We perform calculations for both cases: once for an emitter coupled to the gold antenna and once for an emitter on a glass substrate for reference. To study the excitation process, the setup with and without the antenna is irradiated with a plane wave at a wavelength of $\lambda = 532$ nm. The polarization of the electric field is set to be parallel to the short axis of the antenna, corresponding to our experimental arrangement. We solve numerically Maxwell’s equations and obtain spatially resolved electro-magnetic field at the excitation wavelength. Equating the results for the excitation and the emission processes once in the presence of the nanoantennas and once in the referential situation allows for direct comparison with our experimental measurements as the method used in [164]. All geometrical details considered here are consistent with the experiments.

In slightly more detail, the normalized excitation rate can be calculated as

$$\frac{\gamma_{\text{exc}}}{\gamma_{\text{exc}}^0} = \left| \frac{n_p \cdot E(r_m)}{|n_p \cdot E_0(r_0)|} \right|^2$$  \hspace{1cm} (2.1)$$

where $n_p$ is the unit vector pointing in the direction of the dipole moment and $r_m$ is the location of the dipole emitter. The fields $E(r_m)$ represent the induced electric fields at the location of the dipole emitter in a setup with antenna under plane wave illumination, and $E_0(r_0)$ is the referential induced electric field on the surface of the substrate in a setup without antenna under same illumination. The emission is a result of the exciton recombination, which restricts the electric dipole moment of the emitter to be in the 2D plane of the MoSe$_2$ flake. However the orientation of the dipole moment in this plane is uncertain [179]. We therefore consider an average ‘in-plane’ amplitude of the excitation field at $\lambda = 532$ nm and use

$$n_p \cdot E(r_m) = \sqrt{E_{x}^2(r_m) + E_{y}^2(r_m)}$$  \hspace{1cm} (2.2)$$

in the calculation of the field enhancement.

To characterize the emission process, we then calculate the quantum yield. This quantity is a measure for the quality of the antenna, since it accounts for the non-radiative and internal losses of the hybrid antenna - dipole emitter system. The normalized quantum yield is given by [180]

$$\frac{q_a}{q_a^0} = \frac{\gamma_r}{\eta + (1 - \eta_j) / \eta_j} \cdot \frac{\eta_i}{\gamma_r^0}$$  \hspace{1cm} (2.3)$$

where $\gamma_r$ and $\gamma$ are the radiative and the total decay rate of the emitter, respectively, evaluated at the emission wavelength of $\lambda = 785$ nm. The superscript ‘0’ indicates the quantities calculated without the antenna. The quantity $\eta_j$ is the intrinsic quantum yield of the dipole emitter [164,180]. For a perfect
Manipulation of PL from 2D MoSe$_2$ by plasmonic nanoantenna emitter, it holds $\eta_i = 1$ and the antenna can only reduce the overall system efficiency. For emitters with low $\eta_i$, the overall radiative efficiency can however be effectively increased. For our simulations, we considered $\eta_i = 0.05$ to reflect the fact that MoSe$_2$ is a rather poor emitter. This quantity is estimated by comparison of the experimental emission from flakes of MoSe$_2$ and MoS$_2$ [35] on a glass substrate at the same excitation power. The MoSe$_2$ flake shows approximately an order of magnitude higher PL intensity, therefore we estimate its internal quantum efficiency to be a factor of 10 higher than MoS$_2$ [35]. Note that the quantum yield we used here is just a rough estimation and the actual value is unknown so far, eventually we wish to emphasize that a monolayer of MoSe$_2$ is a rather poor emitter. However, the actual value we assume for the intrinsic quantum yield is of secondary importance considering the fact that a quantitative comparison to the experimental results is not our purpose. This would require spatial averaging of the emission process to reflect the fact that a monolayer MoSe$_2$ covers the entire sparse antenna. And the detailed discussion of quantum yield of monolayer MoSe$_2$ is beyond the scope of this work. In contrast, here we just want to reveal the physical mechanism behind our observed phenomena.

Finally, the fluorescence rate is a product of the normalized excitation rate $\gamma_{\text{exc}} / \gamma_{\text{exc}}^0$ and the normalized quantum yield $q_a / q_a^0$ and is the quantity measured in the experiment:

$$\frac{\text{PL}_{\text{ant}}}{\text{PL}_{\text{sub}}} = \frac{\gamma_{\text{exc}}}{\gamma_{\text{exc}}^0} \frac{q_a}{q_a^0}$$

(2.4)

A sketch of the considered geometry is shown in Fig. 2.6(a). Figure 2.6(b) shows the cross section of the simulation setup as well. The enhancement of the electric field at the excitation wavelength of $\lambda = 532$ nm by the antenna in the plane where the MoSe$_2$ flake locates in experiments is displayed in Fig. 2.6(c). Here, the antenna (top view) is excited by a plane wave. Note that the strongest field enhancement appears at the edges of the antenna.

As mentioned previously, the transition dipole moments of MoSe$_2$ are spatially distributed in the plane and the eventual measurement signal is the result of an ensemble averaging from all the individual positions and orientations in experiments. However, full numerical consideration of such averaging is resource consuming. Furthermore, the averaging will not provide a physical insight on the different mechanisms of PL modifications. Therefore, we chose to provide a qualitative understanding of the experimental results by studying the interaction of emitters placed at a few individual positions, as shown below. For this purpose, we consider two emitter positions relative to the antenna: one at a central position and one at a corner. In the following, we study the dependence of different physical quantities on the spacer thickness, i.e. the distance between the dipole emitter and the antenna. For simplicity and without loss of generality, we use vacuum as spacer material. The electric field intensity of a plane wave for the case with and without the antenna for both locations is shown in Fig. 2.7(a). Please note that the exci-
Numerical modeling

\[eq:2.3\] Simulation results. (a) The excitation rate of the electric field of a plane wave in the characteristic points of the antenna (center [dark blue] and a top-end corner [green]), normalized to the intensity of a plane wave in a setup without the antenna. The illumination plane wave is polarized along the short axis of the antenna as indicated by the inset arrow. (b) quantum yield, (c) fluorescence enhancement, and (d) radiative decay rate enhancement for a dipole emitter placed above the center of the antenna and polarized parallel to its long (dark blue) or short (red) axis; the quantities were calculated also for the case where the dipole emitter was placed above the top-end corner of the antenna and parallel to its long (green) or short (light blue) axis.

The quantum yield, defined via Equation (2.3) is displayed in Fig. 2.7(b).
and the fluorescence enhancement $\frac{\text{PL}^\text{ant}}{\text{PL}^\text{sub}}$ is shown in Fig. 2.7(c). We could see from Fig. 2.7(b) that the quantum yield is enhanced and decreases with increasing spacer thickness when dipoles are at the corner of the antenna for both orientations. When dipole is positioned at the center of the antenna, the behaviors of the dipoles with different orientations are different. For the dipole oriented along the short axis of the antenna, the quantum yield is quenched and changes slightly with increasing spacer thickness. For the dipole oriented along the long axis of the antenna, the quantum yield is quenched when the dipole is very close to the antenna. Then the quantum yield increases with increasing spacer thickness until reaching its peak value at a spacer thickness around 7 nm. Afterward, the quantum yield starts dropping and asymptotically reaches unity. As discussed above, the quantum yield takes the leading role that affects the fluorescence rate which corresponds to the quantity we observed in experiments. So the fluorescence rate shown in Fig. 2.7(c) preserves the trends of the quantum yield with increasing spacer thickness except that the curves are flattened a little bit due to the multiplication with the excitation rate. Since the experimental results are a consequence of ensemble measurements, we could conclude that the quenching effects dominate for the sample in the absence of a spacer. In contrast, for a spacer with a finite thickness the enhancement of the fluorescence can be harvested. We could also infer from the simulation results that the optimum spacer thickness for enhancing the PL is around 7 nm (close to the value we used in experiments). Increasing further the space thickness will not result to more PL enhancement as the emitters interacts weakly with the antenna. Considering the fact that actually a large share of emitters will not be exposed to a spatial region in our experiments where the quantum yield is enhanced, the increase in the fluorescence signal by a factor of three (observed in our experiments) is quite remarkable.

The radiative decay rate enhancement $\frac{\gamma_r}{\gamma_0}$ is often discussed as the measure for the gain of light that the dipole emitter will radiate into the far-field when coupled to the antenna [144]. The radiative decay rate enhancement for our antenna is shown in Fig. 2.7(d). Enhancements by approximately up to two orders of magnitude can be seen. This enhancement in the radiative rate is eventually the reason for the observed increase in the fluorescence rate. Actually, the excited emitter has multiple decay channels. First of all, a very likely path for its de-excitation is the internal non-radiative recombination of the excitons and therefore non-radiative relaxation due to the low internal quantum yield. This quantity cannot be affected by the modified optical environment. Additionally, the dipole emitter can decay through radiative or non-radiative processes via the antenna. Crucially, these are the transition rates that are improved by the plasmonic antenna. The non-radiative decay due to the antenna is certainly undesirable, but it is a price that must be accepted to improve the radiative decay rate.
2.5 Conclusion

We have studied the coupling of monolayer MoSe$_2$ with plasmonic nanoantennas and have demonstrated emission manipulation in such materials from quenching to enhancement mainly through affecting the emission process. This manipulation is achieved by adding a dielectric spacer between the antenna and MoSe$_2$ monolayer. Our experimental results are supported by numerical calculations, which further reveal the coupling mechanisms between the plasmonic antenna and MoSe$_2$ monolayer. In particular, we have observed that the nanoantenna enhances the radiation rate when compared to other non-radiative decay processes, i.e. especially the internal non-radiative decay. To harvest this positive aspect of the nanoantenna requires however to enforce the distance between the MoSe$_2$ and the nanoantenna since otherwise quenching would dominate the processes. This has been clearly seen in our experiments and the observation is fully supported by the numerical simulation. To the best of our knowledge, the present work provides the first study of Au-MoSe$_2$ system, offering more insights into the interaction between the nanoantenna and monolayer MoSe$_2$. Importantly, MoSe$_2$ is a largely unexplored member of the TMDC family, offering several advantages in comparison to its widely studied MoS$_2$ and WS$_2$ counterparts. Moreover, the enhanced PL with unchanged spectrum shape is meaningful for practical MoSe$_2$ applications when considering its spectral stability. Furthermore, PL manipulation in our experiments is realized by affecting the emission process of MoSe$_2$, this method is more robust as it is independent from the excitation scheme, which is especially important for devices with electrical pumping. Besides, enhancement (quenching) effect varying with excitation wavelength is also studied. The method presented here in general offers an important way for PL manipulation in large dynamic range from quenching to enhancement for these advanced materials, as well as the opportunity of polarization-based PL control, both of which are promising for future optoelectronic applications and developments.

Statement


In this work, HC led the projects in sample preparation, PL characterization, data analysis, paper writing. The simulation was done with the help of ER, JS, CR. All other authors contributed to some part of the projects and the discussion.
Manipulation of PL from 2D MoSe$_2$ by plasmonic nanoantenna
Enhanced and directional emission from multi-resonant $WSe_2$-Si hybrid structure

3.1 Introduction

As discussed in Section 1.3, 2D TMDCs show a great potential as atomic-scale versatile light sources, as their electronic structure forms a direct bandgap when the material is reduced to a monolayer [30, 56, 112, 181]. Various important applications such as low-threshold lasers [147, 152, 182], single-photon emitters [74, 77, 183], excitonic light-emitting diodes (LEDs) [80, 87], cascaded single-photon emission [105] and SHG [58, 124, 134, 136, 184, 185] have been demonstrated with these 2D materials. Furthermore, the valley-based emission properties of TMDCs open a new door for information processing and novel helical light emitters [46, 49]. The optical properties of these emitters are also electrically tunable, which makes them suitable for on-chip circuit integration.

On the other hand, enabling light sources in the silicon photonics is an important requirement for on-chip optoelectronic applications [186, 187]. While silicon alone cannot generate the required light, integration with other direct-bandgap materials is being sought. Integration of germanium or III-V materials on silicon faces technical challenges due to a lattice-constant mismatch and different thermal properties [188]. With the desire to overcome such limitations, the integration of 2D TMDCs onto silicon photonic structures emerges as a new promising solution [189, 190]. 2D materials are held together by out-of-plane van-der-Waals forces, and can be transferred onto a silicon substrate without lattice mismatch issues.

However, the emission efficiency of a single layer TMDCs is much less than other direct bandgap semiconductors, which is naturally limited by its sub-nanometer thickness (light-matter interaction length), thus preventing monolayer TMDCs from practical applications. Coupling of 2D mate-
Enhanced and directional emission from multi-resonant WSe$_2$-Si hybrid structure

Figure 3.1: Control of emission from 2D TMDCs by non-metallic structure. (a) PL spectra from different position in a system consisting of GaP photonics cavity and a monolayer WSe$_2$, the inset picture show the top view of system and the position information [150]. (b) PL intensity distribution in the in-plane momentum space taken from a monolayer WSe$_2$ on and off the photonic crystal cavity [150]. (c) Schematic of the proposed silicon-based photonic crystal cavity to enhance the emission intensity and directionality from 2D TMDCs [191]. (d) Simulated confined electric field distribution in the plane perpendicular to silicon rod for the structure shown in (c), two figures show the two in-plane cross-polarized components, respectively [191].

Enhancement and directional emission from multi-resonant WSe$_2$-Si hybrid structure to photonic structures is a promising approach to enhance the light-matter interaction and tailor the emission radiation properties [36, 112]. Indeed, various plasmonic structures have been explored to enhance and engineer the PL and radiation properties from 2D TMDCs [155–157, 160, 192–194]. However, the plasmonic-driven enhancement of emission is very localized to the hot-spots of the nanostructures, and the average enhancement over the entire material remains moderate [193]. Furthermore, the localized hot-spots of plasmonic nanostructures make their coupling to 2D materials highly sensitive to the distance between the emitter and structure, often requiring challenging nanometer-precision positioning. More details could refer to Chapter 2. Non-metallic nanostructures, such as photonic crystal cavities, have also been proposed for enhancing the emission from TMDCs monolayers [150, 191, 195]. Figure 3.1(a) and (b) show the emission spectra and directionality from monolayer WS$_2$ integrated with a GaP photonic crystal cavity, respectively [150]. Figure 3.1(c) show one silicon-based photonic crystal cavity that is proposed to enhance the emission intensity and directionality from TMDCs [191]. Figure 3.1(d) shows the simulated confined electric field from
this structure. However, these schemes rely on cavity modes with a small vol-
ume, again showing overall limited enhancement. More importantly, none of
these demonstrated platforms is directly compatible to the on-chip integration
in modern silicon photonics [131]. A silicon photonics compatible platform
to strongly enhance the collective emission of the entire 2D materials and to
control its directionality is highly desirable.

Here, we demonstrate enhanced and polarization-selective directional PL
emission from monolayer WSe$_2$ by coupling it to a multi-resonant silicon
grating-waveguide structure. The multiple waveguide modes supported by
the structure are engineered to provide enhancement at both excitation and
emission wavelengths in order to achieve an optimal PL output. The dis-
ersion properties of these modes further offer feasibility to simultaneously
control the polarization and directionality of the emission. A significant re-
duction in radiative emission lifetime of WSe$_2$ monolayer is also demonstrated
by time-resolved measurements. Importantly, our approach is fully scalable,
Si-based and thus suitable for on-chip integration. The demonstrated scheme
could be potentially used to fabricate efficient chip-based light sources for var-
ious applications, including single-photon sources for quantum applications
and ultrafast modulation emitters for visible communication.

3.2 Grating-waveguide fabrication and characterization

By engineering the available photonic modes in the environment, the light-
matter interaction strength could be effectively boosted [164]. Generally, the
largest enhancement of the overall PL emission can be achieved when utiliz-
ing photonic structures with multiple resonances that couple to both excita-
tion and emission radiation. We realize such a scheme through integrating
a WSe$_2$ monolayer onto a shallow multi-resonant grating structure inscribed
into a planar silicon waveguide, which supports multiple propagating mode
resonances.

The side view of our experimental arrangement is shown in Fig 3.2a. A
WSe$_2$ monolayer is positioned on top of a grating etched into a planar waveg-
uide made of amorphous silicon (a-Si). The grating periodicity is selected
such that both the excitation laser and the emission couple to available waveg-
uide modes. The grating structure facilitates coupling of the pump light (from
free space, as indicated by the arrow) to a waveguide mode, which increases
the local field intensity at the monolayer position. Thus, the absorption of the
pump light by the WSe$_2$ monolayer is increased and translates to higher ex-
citation efficiency. The emission of WSe$_2$ also couples into waveguide modes
supported by the high-index a-Si layer. Note that due to the amorphous
structure of the silicon layer, it is nearly transparent at the emission wave-
length [185]. The coupling of the WSe$_2$ layer to the silicon waveguide reduces
the radiative lifetime of emission, which in turn is extracted efficiently to free
Figure 3.2: Waveguide-grating structure and its characterization. (a) Schematic side view of the structure under investigation: a monolayer WSe$_2$ is located on top of a grating inscribed into the planar waveguide. Geometrical dimensions, of course, are not to scale. (b) parameters of the grating-waveguide structure (i) and scanning electron microscopy image of a top view of the grating structure used in experiments (ii), part (iii) shows calculated total field profiles at guided mode resonant wavelengths of the grating-waveguide structure for normal incident plane waves. (c, d) Measured and calculated transmittance of the grating-waveguide structure for different linearly polarized light relative to the unpatterned area, respectively. The dashed line shows the measured emission spectrum of WSe$_2$ monolayer.

space due to the grating structure. Therefore, such an experimental scheme offers boosting the PL emission simultaneously through the excitation and emission processes. Furthermore, as the emission couples into different leaky modes supported by the grating-waveguide structure, the emission would be highly directional depending on the dispersion of the modes supported by the structure.

Experimentally, a 200 nm layer of hydrogenated a-Si was deposited on a glass substrate by plasma-enhanced vapor deposition as the waveguiding layer. The hydrogenated a-Si layer was deposited by plasma enhanced vapor deposition at 250 °C. The refractive index and extinction coefficient of the material was measured by ellipsometry afterwards. Then, the grating structure was fabricated by electron beam lithography at 20 kV using the positive resist ZEP-520A. The development was performed by inserting the sample into n-Amyl acetate. The resulting resist pattern was used as an etch mask for a-Si etching in CHF$_3$/SF$_6$ plasma. The residual resist was removed by oxygen
plasma. Details for the samples fabrication are shown in Fig. A.1. Compared to crystalline Si whose absorption starts to increase sharply below 1100 nm, hydrogenated a-Si is transparent up to 700 nm owing to high optical bandgap of 1.73 eV [196]. Hence a-Si was chosen in this work because of its low optical loss at the emission peak of WSe$_2$ around 750 nm. The refractive index and extinction coefficient of the waveguide layer were measured by ellipsometry methods afterwards. In the next step, a binary grating with periodicity of 214 nm and depth of 50 nm designed to facilitate coupling of waveguide modes to radiation and excitation was etched into the a-Si layer. The part (i) of Fig. 3.2(b) shows the designed parameters of the grating-waveguide structure (side view), and the part (ii) shows a scanning electron microscopy image of the top view of the fabricated grating, and the calculated TE$_0$, TM$_0$ and TE$_1$ mode profiles confined by this structure are also shown in part (iii). Figure 3.2(c) shows measured transmittances for different linear light polarizations of the patterned grating relative to the unpatterned area for almost normal incidence, the transmittance is measured from setup shown in Fig. A.2. Multiple resonances arising from the excitation of waveguide modes are visible. The black dashed line shows the measured PL emission spectrum of WSe$_2$ monolayer overlapping with the resonances. Finite-element light scattering simulations for normal incident plane waves were done to confirm the nature of the observed resonances, the results are shown in Fig. 3.2(d). To account for the focusing effect introduced by the objectives used in experiments, we assume that the incoming pump light has an angular distribution that follows a Gaussian shape centered around normal incidence with a standard deviation of 2 degrees. The three resonances can indeed be attributed to TE$_0$, TM$_0$ and TE$_1$ modes supported by the underneath waveguide as labeled, which is discussed in detail below. As shown in the figures, the emission spectrum of the WSe$_2$ overlaps with both TE$_0$ and TM$_0$ resonances. The excitation wavelength could be chosen such that the pump laser couples to the TE$_1$ waveguide resonance, thereby we could enhance excitation and emission at the same time. Furthermore, emission out-coupled from TE$_0$ and TM$_0$ modes will go into defined directions due to their respective dispersive nature and sharp resonance linewidths. Thus, control the emission directionality can be accomplished by tailoring either the periodicity or polarization. One can observe discrepancies in terms of magnitude and line shapes when comparing the numerical and experimental results. We associate these discrepancies to fabrication and measurement uncertainties. However, we wish to note that the simulation still well reproduces the resonant wavelengths and linewidths of the waveguide mode resonances, which is of main importance in the work. The general trend of the relative transmittance spectrum is also captured well.

In deducing the coupling efficiency, we examine the calculated extinction spectra (where extinction is defined as $Ext = 1-T_0$ at normal incidence). One can estimate the coupling efficiency by looking into the peak extinction at resonance and comparing it to the background response in the absence of the resonant contribution. The extinction plot is given in Fig. 3.3 for the grating-waveguide structure (a) and a planar multilayer reference (b). The
Figure 3.3: Calculated extinction and dispersion relation for the grating-waveguide structure. (a, b) Calculated extinction of the grating-waveguide structure for plane wave excitation from air with TM (a) and TE (b) polarization. (c,d) Dispersion relations at $k_x = 0$ for TM (c) and TE (d) waveguide modes. The black dash line indicates the light line in air while the cyan dash line gives the light line in the SiO$_2$ substrate. The solid lines are dispersion of waveguide modes in a reference flat planar air/a-Si/SiO$_2$ waveguide with a-Si thickness of 175 nm, which are flipped into the Brillouin zone assuming a periodicity $P = 214$ nm. The open circles are the leaky guided mode dispersions of our grating-waveguide structure deduced by the resonant mode calculation tools of JCMsuite.

Planar layer response can be considered to be the background extinction response, though one must account that the grating structure would induce a shift to the broad Fabry-Perot features, which is more apparent for the TM case. The peak extinction at the TM$_0$ (720 nm) and TE$_0$ (750 nm) resonant wavelengths is 1. Additionally, since the TM$_0$ and TE$_0$ resonances have relatively sharp linewidths, one can distinguish more easily that the contribution of the background extinction without the resonant is less than 0.1. This is a strong indication that our grating structure provides highly efficient coupling (>90% efficiency) between normal incident plane waves to the leaky guided modes (and by reciprocity from the leaky guided modes to the normal outgoing plane wave). Resonant wavelength of TE$_1$ waveguide mode is in a region where the background extinction is high. However, one can still see that the coupling is fairly strong as a distinct peak is still feasible. The extinction at the TE$_1$ resonant wavelength (640 nm) reaches 0.95 as compared to the background extinction response around that wavelength range 0.725.
One thus see that at least 80% of the power that would’ve otherwise be transmitted to the substrate without the grating structure is loss due to the TE\textsubscript{1} mode excitation. Thus, the coupling efficiency for the TE\textsubscript{1} mode can also be expected to be in the range of 80%. Although one may be ignoring the subtleties of interference effects that can be significant in cases with a strong background response, our conclusion of efficient coupling between radiation and waveguide modes is also supported by the fact that the leaky resonant excitations is observed to cause distinct features in both the relative transmittance and extinction spectra. What’s more, a relation of the leaky waveguide modes’ dispersion sustained by the grating-waveguide system at $k_x = 0$ for $G = 2\pi/214$ nm is calculated in order to provide further clarity on the dispersive nature of the modes. They are shown in Fig. 3.3 for TM (c) and TE (d) modes, respectively.

### 3.3 PL and momentum space characterization

![Figure 3.4](image_url)

**Figure 3.4:** PL enhancement induced by the grating-waveguide structure. (a) Left: optical image of the sample. Right: 2D PL mapping of the sample. (b) PL spectrum of WSe\textsubscript{2} measured from on-grating and off-grating region. (c) Dependence of PL enhancement factor on the excitation wavelength. (d) Time-resolved measurements from on-grating and off-grating region, the pumping laser wavelength is 680 nm.

A monolayer of WSe\textsubscript{2} exfoliated from a bulk crystal was dryly transferred onto the grating. Figure 3.4(a) shows the optical microscope (left) and 2D PL
mapping images (right) of the sample, respectively, where we could observe obvious PL enhancement induced by the grating. The micro-PL spatial mapping were performed on a commercial WiTec alpha300S system in confocal microscope configuration, as shown in Fig. 3.3. Here, we define the PL enhancement factor (PL$_{ef}$) as the average on-grating PL intensity divided by the off-grating value as shown in the formula under Fig. 3.4(a). By exciting the sample with a 633 nm (around the TE$_1$ resonance) He-Ne continuous-wave (CW) laser, we observed up to 8 times enhancement of the PL from the on-grating area compared to the off-grating one. The spectra measured from two different positions (on-grating and off-grating region) are shown in Fig. 3.4(b).

To confirm and distinguish the enhancement effects coming from excitation and emission, we also measured the dependence of the enhancement factor on the excitation wavelength, as shown in Fig. 3.4(c). In these measurements, a Fianium WhiteLase supercontinuum laser was used as excitation source, where 10 nm spectral band has been selected using an acousto-optic filter, under the same average power as for data shown in Fig. 3.4(a). The strongest enhancement happens when the sample is excited by a laser wavelength of around 630 nm, which corresponds to the TE$_1$ resonance of our sample and fulfills our expectation. The overall enhancement factor is slightly weaker than that in our CW experiments, which is due to a broader spectral and pulsed (a few picoseconds) excitation. This experiment also shows the feasibility of tuning the enhancement factor by varying the excitation wavelength.

In addition, time-resolved measurements were conducted to check the emission enhancement as shown in Fig. 3.4(d). For better comparison, here we normalized the emission intensity to its respective maximum and plotted the decay behavior in a logarithmic scale. We also fitted the decay curve into a bi-exponential function [197] shown as solid lines. We could observe that the radiative behavior of WSe$_2$ for the on-grating region is around twice faster than off-grating one, which proves that we harvested emission enhancement from our samples too due to the coupling of the monolayer WSe$_2$ emission into the leaky waveguide modes. Note that the decay curves are not straight lines (on a logarithmic scale), which is likely because there are multiple recombination processes involved in the emission [197]. However, the detailed study of the dynamics of carriers is beyond the scope of this work. Also, we found that the decay lifetimes of the delays were in the range of tens of picoseconds, which offers the opportunity for ultrafast modulation with speed up to 50 Gbps. Thus, we conclude that our multi-resonant Si grating-waveguide structure could effectively enhance PL of a WSe$_2$ monolayer averagely up to 8 times by combing both the excitation and emission enhancements.

To further explore the coupling between the monolayer WSe$_2$ and grating-waveguide structure, we investigated the far-field angular emission from our system. Near- and far-field analyses are done using the finite element solver JCMsuite (JCMwave, Germany) [198]. In-plane momentum ($k_x$, $k_y$) distribu-
§3.3  PL and momentum space characterization

Figure 3.5: Experimental back-focal plane images of emission from monolayer WSe$_2$. A notch filter with half maximum bandwidth of 10 nm centered at 750 nm was used to filter out the spectrum. (a) The overall emission from on-grating WSe$_2$, (b, c) the back-focal plane images of the emission component polarized perpendicular ($I_y$) and parallel ($I_x$) to the grating ridge from the on-grating WSe$_2$ structure, respectively. (d) Back-focal plane image of the total emission from off-grating WSe$_2$ structure.

The in-plane momentum is related to the emission polar angle $\theta$ through the relation $\sin(\theta) = k_{||}/k_0$, where $k_{||} = |k_x + k_y|$, and $k_0 = 2\pi/\lambda$ is the wave vector amplitude at wavelength $\lambda$. We observed quite different emission patterns from the on-grating and off-grating regions. Figure 3.5(a) shows the back-focal plane image of the total emission from the on-grating regions, where we observe that the emission goes preferentially into four distinct angular regions. In contrast, the back-focal plane image of emission from unpatterned regions, shown in Fig. 3.5(d), displays typical pattern with intensity decaying...
from the center. Furthermore, we mapped the back-focal plane imaging of the emission of different polarizations. Figure 3.5(b) and 3.5(c) show the emission patterns when a polarizer oriented across and along the grating ridge was applied in the detection path, respectively. These two images show clearly that the emission direction is polarization-dependent. Therefore, the emission directionality and intensity in the grating region can be tailored with a polarizer to a great degree.

Figure 3.6: *Experimental setup for PL characterization from monolayer WSe$_2$. M1, M2, M3 and M4 are removable mirrors. We can switch between femtosecond and He-Ne 633 nm lasers for excitation by removable mirror M1. Mirror M2 can switch between white light illumination and laser excitation, white light here is used to locate the sample. M3 can switch between CCD imaging and spectral measurements. M4 can switch between integrated and time-resolved spectral measurements. L1, L2, L3 and L4 are lens. L1 is in a removable mount, which could switch between real-space and back-focal-plane imaging. BS refers to beam splitter, Ob is objective. P1 is polarizer and $\lambda/2$ is half waveplate, which are used to tune the excitation polarization. P2 is another polarizer that is used to distinguish different polarization components of the emission. Spectro refers to spectrometer. The streak camera is triggered by the femtosecond laser.*

All the PL spectral measurements and back-focal-plane imaging were conducted on an in-house microscopy system as shown in Fig 3.6 schematically. A 100× objective with numerical aperture of 0.7 was used for excitation and collection of emission in reflection configuration. A 633 nm He-Ne continuous-wave was used as excitation source for integrated spectral and back-focal-plane imaging. A pair of lenses were used to translate the back focal plane of the imaging objective to a CCD camera. An Optronis SC-10 streak camera triggered by Coherent Chameleon Ultra II Femtosecond laser with resolution down to 2 ps was used for time-resolved measurements, the sample is also excited by the Femtosecond laser at a central wavelength of 680 nm, with a repetition rate of 80 MHz and a pulse duration of 140 fs.
3.4 Numerical simulation

To investigate further the physical mechanism behind the measured PL characteristics, we performed numerical simulations of the emission of a WSe$_2$ monolayer coupled to the grating-waveguide structure. The WSe$_2$ monolayer emission is modeled as a superposition of different electric dipole emitters, placed 1 nm above the grating, for three different lateral positions: in the center of the unit cell (this corresponds to the position above the center of the ridge), above the edge of the ridge (this corresponds to the position at 58.5 nm from the center), and close to the boundary of the unit cell (corresponding to the position which is almost above the center of the trench). As the WSe$_2$ monolayer does not support out-of-plane oriented dipole moments, we only simulated in-plane oriented electrical dipoles, oriented across ($y$-direction) and along ($x$-direction) the grating ridge. Typically, simulating a single dipole emission in a periodic system requires one to consider a large amount of unit cells, which in full three dimensions is computationally time consuming. To handle this, we utilize a supercell algorithm which allows us to deduce the singular dipole emission response in a periodic system by combining single unit-cell simulations with varying phase relations along the periodic boundaries.

For the far-field calculation of a singular dipole emission near the grating-waveguide structure, we utilized unit cells consisting of a 200 nm thick substrate of SiO$_2$ and the a-Si grating with a 150 nm thick guiding layer and the 50 nm thick ridge on top. Above the grating is air (refractive index $n = 1$). As upper and lower boundaries of the unit cell, we place Perfectly Matched Layers (PMLs) that attenuate the field to suppress reflections at the computational domain boundaries. The horizontal width of the unit cell is 214 nm and the width of the ridge is 107 nm. Periodic boundary conditions are used in the $x$- and $y$-direction. Each simulation of a unit cell with periodic boundary conditions implies that an infinite number of periodically arranged dipole sources with a certain phase relation between them are considered. By performing inverse Floquet transformation, which superpose the solutions for different periodic phase relations of the single unit cell results, we reconstruct the field of a singular dipole in a periodic system. 128 supercells are used as a compromise between accuracy and computational time.

The simulated far-field distribution in momentum space, averaged over the positions and orientations, is shown in Fig. 3.7(a). Good matching of the singular dipole far-field calculations and the measured momentum space of the emission is obtained, when compared with Fig. 3.5(a). By considering only the far-field component perpendicular to the grating ridges [Fig. 3.7(b)], we reproduce the main features in Fig. 3.5(b), in which there is high peak intensity around $k_y \approx \pm 0.3k_0$. Conversely, considering only the intensity component parallel to the grating ridges [Fig. 3.7(c)], allows us to reproduce the features of Fig. 3.5(c).
The observed polarization-selective directional emission property is linked to the waveguide modes the emitters couple to. To demonstrate this, we calculated the dispersion relation of TE\(_0\) and TM\(_0\) waveguide modes for a flat slab waveguide system (air/175nm a-Si/SiO\(_2\)) folded into the first Brillouin zone with a grating vector \(G = 2\pi/214\) nm [Fig. 3.5(d)]. The folded \(k\)-space cross-section of the waveguide mode dispersion leads to four curves related to \(\pm 1\) diffraction coupling of radiation to the TE\(_0\) and TM\(_0\) waveguide modes. These four curves match well with what was observed in the experiments and far-field simulations, which indicates that these are indeed the modes...
that the monolayer is coupling to. In addition to the folded dispersion curves, we show intensity plots obtained from 2D finite element simulations of a line dipole emission above the grating-waveguide and the flat multilayer structure [Fig. 3.8(a) and 3.8(b)]. As a-Si is not absorbing in the emission wavelength, the waveguide modes in the grating-waveguide region have a long propagation range. Due to this, one would have to account for the contribution of many unit cells of the periodic system. Here, we show simulations assuming 100 unit cells with the line dipole source placed in the center of the central unit cell. Figure 3.8(a) shows the intensity profiles when the dipole line source is polarized along the grating ridges, which thereby excites TE waves. As can be seen in the intensity plots, a major portion of the emission couples to the waveguide modes for both the case with and without grating. Efficient coupling of the emission to the waveguide modes can also occur when the dipole line source is polarized along the y-direction, which excites TM waves [Fig. 3.8(b)]. Since efficient coupling of the emission to the waveguide modes occurs, one can expect that the radiation properties would be dictated by the waveguide modes’ radiative nature if their outcoupling is facilitated. Without the grating structure, however, a large portion of the emission that couples to the waveguide mode remains guided and does not affect the angular distribution of the detected PL signal.

Having discussed the origin of the polarization dependent directionality, we proceed to examine the photonic effects which provide enhancement at the...
emission wavelength. We calculate the average ratio of total emitted power by point dipoles in the grating-waveguide system relative to the flat case with the expression \( \frac{P_{\text{tot}}^{\text{grat}}}{P_{\text{tot}}^{\text{flat}}} \), where \( P_{\text{tot}}^{\text{grat}} \) indicates the total emitted power in the grating structure and \( P_{\text{tot}}^{\text{flat}} \) the total emitted power of the flat structure with a thickness of the a-Si layer of 200 nm. For the dipoles polarized across the grating, we obtained a ratio of 1.5, which is comparable to the measured lifetime enhancement indicating that the emission process is dominated by spontaneous emission and thus contributions of different dipoles to the PL can be summed up in an incoherent manner. For the dipoles polarized along the grating, we only get a ratio of 1.01, which suggests that they have a longer lifetime in the grating system than the dipoles polarized across the grating.

To calculate the outcoupling enhancement, we compare the total dipole emission power \( P_{\text{tot}} \) with the power radiated into air, \( P_{\text{rad}} \), both for the grating structure and the flat structure. From our simulations, we get \( \frac{P_{\text{rad}}^{\text{grat}}}{P_{\text{tot}}^{\text{grat}}} = 0.26 \) and \( \frac{P_{\text{rad}}^{\text{flat}}}{P_{\text{tot}}^{\text{flat}}} = 0.11 \). This means that the portion of power outcoupled into air in the grating system is by a factor of \( 0.26/0.11 = 2.36 \) larger than in the flat system. Even when this outcoupling enhancement factor is multiplied by the calculated life time enhancement factor (\( \times 1.5 \)), the result does not match the PL enhancement factor obtained in the measurement. This enhancement factor mismatch indicates that the grating structure does not only enhance the emission.

To further confirm the absorption enhancement of the pump light, which can contribute to the PL enhancement, we calculate the intensity enhancement 1 nm above the grating ridge for TE polarized light for different excitation wavelengths relative to a flat unpatterned multilayer slab. We consider plane waves incoming to the structure from air at different inclination angles as done in Fig. 3.2(d). The angle-averaged intensity enhancement for the wavelength range 500 nm to 700 nm is plotted in Fig. 3.8(c). An intensity enhancement peak around the wavelength of 640 nm is visible in agreement with the measurement in Fig. 3.4(c). The intensity enhancement peak is due to the excitation of a TE\(_1\) mode as shown by the inset figure, which shows the calculated field intensity for normal incident plane wave. Our simulations further show that one can obtain a peak intensity enhancement reaching 6 times around 640 nm due to the TE\(_1\) mode excitation, which can be expected due to a also roughly 6 times maximum increase of absorption by the WSe\(_2\) monolayer. Further engineering of the mode profile by the grating shape or the placement of the emitter can potentially increase this even more.

3.5 Conclusion

We have demonstrated enhanced and polarization-selective directional emission from monolayer WSe\(_2\) integrated onto a Si grating-waveguide structure.
The PL enhancement and directionality have been realized by simultaneously coupling the emission and the excitation fields into the resonant modes supported by the structure. By tailoring the resonant frequencies and dispersion of the waveguide modes, we have shown great flexibility in controlling the WSe$_2$ monolayer emission in both intensity and directionality. Furthermore, our time-resolved measurements show that our structure could effectively reduce the lifetime of the radiation decay, which provides opportunities for ultrafast modulation up to 50 Gbps. In addition, our numerical simulations have revealed how different modes contribute to the emission enhancement and directionality, and the numerical results explain experimental data well. These findings, demonstrated on fully scalable Si-based platform, are important for chip-integrated optoelectronic applications of 2D materials.

Statement

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In this work, HC led the projects in idea conceiving, sample preparation, PL characterization, data analysis, paper writing. YJ contributed to the sample preparation and PL characterization parts. The simulation was done with the help of SN, AA, CR. All other authors contributed to some part of the projects and the discussion.
Enhanced and directional emission from multi-resonant WSe$_2$-Si hybrid structure
Valley-based directional emission from monolayer WSe$_2$ mediated by nanoantenna

4.1 Introduction

As discussed in Sec. 1.3.2, the inversion symmetry breaking and quantum confinement of the 2D TMDCs, especially in monolayer form, offer unprecedented opportunities to explore valley-based physics and applications [36, 43, 112]. Valley pseudospin refers to degenerate energy extrema in momentum space [36]. In 2D TMDCs, which have a hexagonal lattice structure, valleys of degenerate energy locate at the corners of the hexagonal Brillouin zone: the K and K’ points [26, 200]. Analogy to spintronics, valley pseudospin could also be potentially used as non-volatile information storage and processing, which is known as valleytronics [201–205]. Thus, it can be envisioned that the dynamic excitation and control of carriers in different valleys is crucial for future valley-based information technologies and applications.

In particular, monolayer TMDCs with direct bandgap at the K and K’ points [35] makes it possible to control the valley freedom optically. Pumping of exciton of valley polarization have been demonstrated by polarization-resolved PL measurements [45–47]. And we reproduced the main features of these findings, Figure 4.1(a) shows the experimental setup used for polarization-resolved PL measurements, Figure 4.1(b) shows the optical images of the monolayer WSe$_2$ sample we used in experiments (left) and schematic of the valley selection rule of the emission (right). Figure 4.1(c) shows the polarization-resolved emission when the sample is excited by different circularly polarized laser, where we could observe that left- (right-) handed circularly component dominates the emission when excitation is left (right) circularly polarized.

Based on these findings, valley-based light emitting diode with controllable emission polarization [110], valley Hall effect [52], valley-dependent photogalvanic effect have all been explored. Besides, excitonic valley coher-
Valley-based directional emission from monolayer WSe$_2$ mediated by nanoantenna

Figure 4.1: Optical excitation of valley polarization. (a) Experimental setup built for characterizing the valley polarization from a monolayer WSe$_2$. (b) Left: the optical image of the WSe$_2$ sample exfoliated from bulk crystal used in experiments; middle: schematic of the monolayer WSe$_2$ and the first Brillouin zone structure; right: schematic of the valley-selection rules. (c) Polarization-resolved measurements of PL from a monolayer WSe$_2$ under right/left circularly polarized light excitation.

ence [49], valley- and spin-polarized Landau levels [115] and valley Zeeman effect [116–119] have all been studied in monolayer TMDCs too. Different schemes have been developed, such as optical [120, 121], magnetic [104, 122] and electrical [49, 206], to control the valley pseudospin in 2D TMDCs, a few examples are shown in Fig. 4.2

On the other hand, to facilitate device integration, it is preferable that
Figure 4.2: Control of valley polarization. (a) Circular polarization degree of excitonic PL from a monolayer WSe$_2$ as a function applied magnetic field in Faraday geometry. Each line shows a different orientation of the magnetic field denoted by $\alpha_B$, which is shown in part (ii). Part (iii) shows the inverse width $1/B_{1/2}$ as a function of the $\cos(\alpha_B)$, solid line is the linear fit [122]. (b) Degree of PL polarization as a function of applied magnetic field for exciton (i) and trion (ii), respectively [104]. (c) Rotation-induced PL anisotropy $S_2$ as a function of the excitation-control delay time $\tau$, which indicates that the intervalley decoherence time of a monolayer WSe$_2$ is in the range of hundreds of femtoseconds [120]. (d) Degree of PL polarization from a bilayer MoS$_2$ at 648 nm as a function of the gate voltage [206].

Light emission from 2D TMDCs can be controlled at the nanoscale. Recent advances in resonant metallic nanostructures, dubbed plasmonic nanoantennas, have shown such great capability and flexibility [30, 36, 112]. Plasmonic nanoantennas could significantly modify the emission of a localized emitter at the nanoscale when the plasmonic modes in the antennas are excited [164, 207, 208]. In particular, other than the fundamental dipole mode, localized emitters could effectively excite the higher-order modes in nanoan-
Valley-based directional emission from monolayer WSe$_2$ mediated by nanoantenna that are in general weakly coupled (or uncoupled) to plane wave excitation [209,210]; the near-field and far-field interference of multiple plasmonic modes offers nanoantennas unprecedented capability to control the emission of localized emitters in various aspects [210,212]. Although previous studies have shown designs for spin-dependent directional emission, their local response is still limited to linear polarization [212], and thus cannot be employed to control the emission of a localized emitter that emits circularly polarized light.

Here, we propose a plasmonic nanoantenna-TMDC system that can effectively route light emission from different valleys of TMDCs into opposite directions. The nanoantenna can support electric dipole and electric quadrupole resonances, and they can only be excited by localized dipole emitters with orthogonal dipole moments. Due to the intrinsic $\pi/2$ phase difference between the electric dipole and electric quadrupole emission, the scattering direction becomes spin-locked when the nanoantenna is coupled to circular emitters. This valley-based scheme could provide useful insight for component design such as coupler and router for the future valley-based information processing system.

### 4.2 Antenna design principles

At resonances, the far-field radiation of nanoantenna could be expanded into multipolar series, Equation $4.1$ shows the first three terms, the electric dipole $\mathbf{p}$, the electric quadrupole $\hat{\mathbf{Q}}$, and the magnetic dipole $\mathbf{m}$, in Cartesian coordinate system [213]

$$
\mathbf{E}(\mathbf{r}) = \frac{k_0^2 e^{i k_d r}}{4 \pi \varepsilon_0 r} \left\{ [\mathbf{n} \times (\mathbf{p} \times \mathbf{n})] + \frac{i k_d}{6} [\mathbf{n} \times (\mathbf{n} \times \hat{\mathbf{Q}})] + \frac{1}{v_d} (\mathbf{m} \times \mathbf{n})... \right\} 
$$  \hspace{1cm} (4.1)

where $k_0$ and $k_d$ are the wave number in free space and medium respectively, $v_d$ is the light speed in medium, $\mathbf{n}$ is the unit vector in the direction of emission, $\mathbf{r}$ is the coordinate vector, $r = |\mathbf{r}|$.

From Eq. $4.1$ we could see that the far-field radiation is in phase with electric dipole moment, while there is a $\pi/2$ phase difference for electric quadrupole. Thus, there is naturally a $\pi/2$ phase difference between the electric dipole and quadrupole emission when their corresponding charges oscillate in phase, and the parallel components of electric dipole and electric quadrupole emission (strictly speaking, quadrupole is a tensor, while parallel is between two vectors) will interfere with each other depending on their relative phase and amplitude. When the amplitudes of the far-field compo-
tent are comparable, the interference will be constructive in one direction and destructive in the other direction when the phase difference between electric dipole and quadrupole is $\pi/2$ or $3\pi/2$, while the interference is prevented if the phase difference is 0 or $\pi$. Our design is based on this interference property to tailor the emission directions from different valleys.

![Diagram of antenna design principles](image)

Figure 4.3: Design principles of the directional emission from different valleys. (a) The proposed scheme to separate emission from different valleys through integrating with properly designed nanoantennas, the directions of the emission from monolayer TMDCs depend on the polarization states of the excitation (different valleys are addressed). (b) Principles of the interference between electric dipole and quadrupole, the direction of constructive interference depends on the relative phase difference between the dipole and quadrupole.

The basic structure of our system is shown in Fig. 4.3(a), the emission from different valleys is directed into defined directions by integrating the 2D TMDCs layer onto well designed nanoantenna. When the system is excited by light of different polarization states, the emission goes into different directions, thus offering us great freedom to control the emission from distinct valleys, which could in potential act as information carrier. Here, we use interference of multiple modes excited in the nanoantennas to realize such functionalities. The general concept of how the nanoantenna works is shown in Fig. 4.3(b). Parallel electric dipole and quadrupole will interfere with each other depending on their relative phase and amplitude, the interference will be constructive in one direction and destructive in the other direction when their phase difference is $\pi/2$ or $3\pi/2$, while the interference is prevented if the phase difference is 0 or $\pi$. Thus, by changing the phase difference of the dipole and quadrupole from $+\pi/2$ to $-\pi/2$, we could tune the radiation direction from one to the other effectively. On the other hand, emission from TMDCs monolayer solely comes from the in-plane exciton or trion, and the exciton could be generally treated as dipole emitter when interacting with photonic structures. So we use two in-plane dipole emitter to represent emission from the 2D monolayer, $+\pi/2$ or $-\pi/2$ phase difference are applied to mimic the left or right circularly polarized emission from exciton in different valleys. To demonstrate our idea clearly, we start with a simple nanoantenna design consisting of two bars.
4.3 Numerical calculation of two-bar antenna

Figure 4.4: Characteristics of the bar antenna excited by dipole emitter (a) (i) side view of the simulation setup; (ii, iii) top view of the short bar and and long bar, respectively. The red arrows represents point dipole emitter with different orientations. The red spots represent electric probes. (b, c) The electric field intensity and phase at the position of probe when dipole emitters with different orientation are used as excitation source for short and long bar, respectively. We only show phase information for short bar excited by horizontal emitter and long bar excited by vertical emitter. The field intensity is normalized to larger one for emitters with different orientations. (d) Azimuthal polar plot of the total ($P_0$) and azimuthal component ($P_\theta$) of the far-field power distribution when the short bar is excited by horizontal emitter. (e) Azimuthal polar plot of the total ($P_0$) and azimuthal component ($P_\theta$) of the far-field power distribution when the long bar is excited by vertical emitter. The direction of $\theta$ is illustrated by arrows.

Different plasmonic modes could be excited in a bar antenna when a localized emitter is placed in the proximity of the bar, depending on a couple of factors such as the antenna size, emitter position and orientation. By choosing proper size parameters, either the dipole mode or the ‘dark’ quadrupole mode of the bar antenna could be excited dominantly by a local dipole source. We choose a short bar with length $L_p=104\, \text{nm}$, width $W_p=25\, \text{nm}$, and a long...
bar with length $L_q=310$ nm, width $W_q=70$ nm, the height of the two bars are both 40 nm. The general side view of our simulation setup is shown in part (i) of Fig. 4.4. Point dipole emitters are placed 5 nm above the antenna in Z direction. To mimic the experimental practice, we simulate the antenna on top of glass substrate. Two electric dipoles with horizontal ($D_h$) and vertical ($D_v$) orientation are placed 25 nm away from the bar antenna in Y direction. Electric probes are located at one end of the bar antennas to detect the electric phase and amplitude. The setup for short bar and long bar antenna are shown in part (ii) and (iii) in Fig. 4.4, respectively.

We start by studying the individual response of the two bar antennas to local dipole emitter orientated along or across the bar by numerical calculations using finite-integral frequency-domain simulations (CST Microwave Studio) with open boundary conditions. To avoid unphysical sharp edges, we model the antenna as rounded corners with a radius of curvature of 5 nm. The considered gold properties are based on experimental data from [177] for the permittivity of gold in the visible/near-infrared spectral region.

The intensity of the electric field along X direction ($I$) and phase information ($\phi$) at the probe position when the structure is excited by local dipole emitters of different orientations, for short bar and long bar, are shown in Fig. 4.4(b) and (c), respectively. For better comparison, we normalize the field intensity to the stronger one. As can be seen in Fig. 4.4(c), for the short bar, the field induced by the horizontal dipole emitter ($I_h$) dominates at the wavelength range we are interested in. In contrast, the excited field from the vertical dipole emitter ($I_v$) dominates for the long bar. What’s more, both of the electric field intensity profiles show a resonant peak around 715 nm. The phase information detected by the probes corresponds to the phases of the oscillating charges, which defines the phases of the dipole and quadrupole moments. The phase information under the dominant excitation, labeled as $\phi_h$ and $\phi_v$ are also shown in Fig. 4.4(b) and (c). We could observe that the two resonant modes are in phase, thus the far-field radiation will have a phase difference of $\pi/2$. To further investigate the nature of the excited modes in the two antennas, we monitor the far-field radiation pattern of the horizontal emitter with short bar and vertical emitter with long bar at the resonant wavelength, which are shown in Fig. 4.4(e) and (f), respectively. Due to the existence of the substrate, most of the emitted power goes into the high-index medium (lower half space). In the case of horizontal emitter with short bar antenna [Fig. 4.4(e)], the radiation pattern shows a typical dipole profile, while the emission shows quadrupole profiles for the case of vertical emitter with long bar [Fig. 4.4(f)]. Besides, we show polar plot for both the total power ($P_0$) and the azimuthal power component (power contributed from azimuthal electric field, $P_\theta$). As can be observed from both Fig. 4.4(e) and (f), the azimuthal component ($P_\theta$) dominates in both cases, which are expected for both dipole and quadrupole radiation from bar antennas along the X direction. By examining the vectorial field profile in the near-field, we further confirm that the electric dipole mode is excited dominantly by the horizontal emitter.
When two dipole emitters are placed near the center of short bar, while the electric quadrupole mode excited by the vertical emitter is dominant for the long bar. Here we fine tune the geometries of the antennas in order to have them resonate around 715 nm, since it matches our experimental results of the peak emission wavelength of the monolayer WSe$_2$. The parameters of the two bars are further optimized such that the radiated far-field electric fields have comparable intensity.

![Diagram of double-bar antenna configuration](image)

**Figure 4.5: Features of double-bar emission.** (a) Schematic side and top view of the double-bar antenna. $\Delta \phi$ represents the phase difference applied between the horizontal and vertical dipole emitter. $\Delta \phi = \pm 90^\circ$ is used to mimic left or right circularly polarized emitter, respectively. (b) Side view of far-field pattern when $\Delta \phi = \pm 90^\circ$ is applied. (c, d) Azimuthal polar plot of the total ($P_0$) and azimuthal component ($P_\theta$) of the far-field power distribution, respectively. We show both cases of $\Delta \phi = \pm 90^\circ$.

After investigating the response of the individual bar antennas, we perform simulation for the combined system consisting of two bar antennas and local dipole emitters, the side and top views of the setup are shown in Fig. 4.5(a). The gap between the two bars is set as 50 nm, and the dipole emitters are located in the center of the gap. To mimic the circular emitters, we implement a phase shift between the horizontal and vertical dipole emitters denoted as $\Delta \phi$, where $\Delta \phi = \pm 90^\circ$ represents right or left circular emission from the emitters. The total radiation pattern (side view) are shown in Fig. 4.5(b) when $\Delta \phi = 90^\circ$ or $-90^\circ$ are applied, respectively. Due to the interference of the fields from electric dipole and electric quadrupole, the original mirror
symmetry of the radiation pattern breaks when a circular emitter presents. Importantly, the directionality could be tuned by changing the sign of the phase difference (circular polarization states) effectively. Figures 4.5(c) and (d) compare the polar plots of the total ($P_0$) and azimuthal power component ($P_\theta$) distribution, it is clear that the azimuthal power component still dominates (the two figures are plotted in same unit), which confirms that the directional emission is mainly contributed by the interference between the dipole modes from short bar and the quadrupole mode from long bar. To quantify the observed directionality, we define the front-to-back ratio (F/B) as ratio between the total power emitted in one half space to the other. The value is 4.7 dB for the total radiation, and 6.0 dB for the azimuthal power component, which could be distinguished by adding a polarizer in experiments. The directionality of the total radiation is slightly weaker than the azimuthal component because some other weaker modes are excited from the long bar as well. Since the valley polarization of the emission from monolayer TMDCs depends on the polarization states of the pumping laser, we could easily tune the emission directionality from different valleys just by changing the pumping polarization states in our TMDC-nanoantenna system.

Furthermore, we evaluate the emission enhancements brought by the plasmonic nanoantennas. The radiation enhancement is defined as the total power radiated by the two dipole emitters coupled to antennas, normalized to the case with no antennas. We find that the radiation is dramatically enhanced up to 15 times at the resonant wavelength. In addition, we check the robustness of this design with regards to spectrum, and we find the directionality preserves from 680 nm to 750 nm. This broadband response makes it suitable to control the emission from monolayer TMDCs such as WSe$_2$ in whole emission range. Thus, the simple nanoantenna we propose here could effectively enhance the emission intensity and tune the valley-based emission directionality from TMDCs.

As discussed, the modes excited by the local dipole emitters depends on the position of the emitters. To evaluate the average directionality offered by our proposed two-bar antenna, we perform scanning of position of the dipole emitters, two cases are taken into account. Firstly, we investigate the average directionality when the emitters are inside the gaps between the two bars by taking 3 positions inside the gap as shown in Fig. 4.6(a). We simulate the cases of emitters at the 3 positions separately and then add up the radiation power, the polar plot of the total power and azimuthal power component are shown in Fig. 4.6(b) and (c), respectively. They show similar patterns as the case of central position, while the front-to-back ratio decreases a bit after averaging due to that the positions away from the center do not have directionality as good as the center position. However, the average directionality still keeps 3.4 dB for the total power and 4.2 dB for the azimuthal power component. Unfortunately, after averaging over more positions outside the gaps [we take 9 typical positions as shown in Fig. 4.6(d)], the directionality degrade a bit more, but we can still tune the emission direction by change the phase shift between
Valley-based directional emission from monolayer WSe$_2$ mediated by nanoantenna

Figure 4.6: Average emission pattern. (a) Schematic of the 9 emitter positions used to evaluate the average effects. (b, c) Azimuthal polar plot of the total ($P_0$) and azimuthal component ($P_\theta$) of the far-field power distribution after averaging over all the positions.

the two emitters (equivalently changing the excitation polarization states for the TMDCs). However, with the development of materials fabrication techniques, nanostructure of TMDCs [217–219] could be fabricated efficiently, so we can control the position and size of the TMDCs. Thus, a system consisting of the bar antenna and TMDCs nanosheet only inside the gap between the bars could in principle serve as efficient light source with tunable emission direction.

4.4 Discussion and conclusion

To further understand our system and seek for ways to improve the average directionality. We compare the total radiation power by the emitters across different positions as shown in Fig. 4.6(d). The central position, where we observe best directionality, emits 2 to 5 times stronger than other positions. The average directionality could be better if the central position had a much stronger emission power. Indeed, directional emission from local emitters en-
abled by plasmonic nanoantennas is highly sensitive to the position of the emitters [210, 214]. To improve the directionality, we do need structures with very strong ‘hot’ spots and the emission shows good directionality when the emitters are located at the spots. This might direct us to further improve our structures by introducing antenna shape like bowtie [220] or split-ring-resonators [214]. However, such structures have more geometric parameters and more complicated modes when excited by local emitters, the process to find the optimized geometric size are difficult and time consuming. Moreover, more complicated structures requires demanding fabrication efforts in practice. In contrast, the bar antenna we propose has simple mode profiles and easy to optimize the size, and the fabrication process is relatively straightforward.

In conclusion, we proposed a paradigm to control the emission intensity and direction from valleys in monolayer TMDCs using multimode plasmonic antennas. We designed a nanoantenna based on two gold bars, of which the dipole and quadrupole modes can be excited dominantly at the same frequency. The interference between the dipole and quadrupole modes results in directional emission, and the direction depends on the phase difference between these two modes. By mimicking the circular emission from valleys in TMDCs with circular dipole emitters, we have shown that the emission (left circular or right circular) from different valleys can be directed into opposite directions when the emitters couple to the two-bar nanoantenna, with a directionality of up to 6 dB, and a radiation power enhancement of up to 15 times. In addition, we discussed the reasons for the degrading directionality when averaging over different positions and proposed the methods to address this issue either by structuring the materials or by designing new structures. The nanoantenna we proposed here could be potentially useful in future valley-based devices, such as imaging and light information processing.

Statement

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In this work, HC led the projects and did all the simulation work, ML, LX and DNN contributed to the discussion.
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Chapter 5

Enhanced Second-harmonic Generation (SHG) from 2D WSe$_2$ in guided-wave geometry

5.1 Introduction

Monolayer TMDCs exhibit advanced optoelectronic properties as discussed in above sections, which include, but are not limited to direct bandgap, robust valley polarization and strong electric tunability. These properties have opened opportunities for a number of applications, including ‘flat-land’ emitters [35, 165, 221] and valley-based applications [46, 47, 49]. Especially, nonlinear optical wavelength conversion of two-dimensional (2D) TMDCs and in particular SHG has attracted lots of attention [124, 125, 134, 136, 136, 222–224], as these 2D materials are intrinsically non-centrosymmetric. Extraordinary strong SHG has been reported for various materials such as monolayer WSe$_2$ [225] and MoS$_2$ [124, 134, 226]. In Section 1.3.3, we also introduced how SHG from 2D TMDCs could be tuned by pumping [58] and electrical gating [114], and how it could be used as useful tools for determining the the crystal properties and orientation [125, 132–134]. However, the sub-nanometer monolayer thickness of such monolayer materials limits the length of their nonlinear interaction with light, and thus the overall conversion efficiency. Thin gold film substrate [227] [Fig. 5.1(a)], optomechanical cavity [223] [Fig. 5.1(b)], microcavity [228] [Fig. 5.1(c)] and photonic crystal cavity [229] [Fig. 5.1(d)] have been demonstrated to enhance the SHG from MoS$_2$ layers [227]. But, in all experiments to date, the 2D materials are excited along the normal of the monolayer, hence the overall nonlinear conversion efficiency is still limited by the sub-nanometer nonlinear interaction length with light, thus preventing their future practical application. Besides, these approaches are either not compatible with the widely used silicon-based platform or require complex fabrication and positioning skills.

On the other hand, silicon photonics plays a crucial role in modern photonic technologies, including a number of nonlinear applications for frequency
Figure 5.1: SHG enhancement from 2D TMDCs by photonic integration. (a) SH signal from a monolayer MoS\textsubscript{2} on SiO\textsubscript{2}/Si substrate and 17nm MoS\textsubscript{2} layer from Au/SiO\textsubscript{2} substrate, the upper inset shows the sample images and the lower inset shows the Raman spectrum of single-layer MoS\textsubscript{2} on SiO\textsubscript{2}/Si substrate \cite{227}. (b) Schematic image of the optomechanical platform with double resonance used to enhance SHG from a monolayer MoS\textsubscript{2} (left) and the SHG from on- and off-cavity regions (right) \cite{223}. (c) Schematic representation of the microcavity designed to enhance SHG from 2D MoS\textsubscript{2} \cite{228}. (d) Illustration of structure of how the photonic crystal cavity is used to enhance the SHG from a monolayer MoS\textsubscript{2} \cite{229}.

conversion and signal processing. However the centrosymmetric properties of silicon inhibit any second order (or $\chi^{(2)}$) nonlinear effects, such as SHG, thus limiting the range of possible applications \cite{230,232}. Various hybrid integration approaches for incorporating non-centrosymmetric materials in the silicon photonics platform have been suggested \cite{188} in order to achieve second order nonlinearity \cite{231}, however with very limited success. The 2D TMDCs can likely provide a viable solution for integration within the silicon photonics platform due to their strong Van der Waals interactions to surfaces. Furthermore, due to their ultrathin nature the integration with Si waveguides will not be disturbing the waveguide modes \cite{233} or hindering other functionalities. However, the integration of 2D TMDCs with Si waveguides and the demonstration of second order nonlinear effects, such as SHG, has not been demonstrated to date.

Here, we develop a monolayer MoSe\textsubscript{2} Si-waveguide integrated, scalable platform for second order nonlinear effects in silicon photonics and experimentally demonstrate strong SHG enhancement in comparison to free-space
SHG from TMDCs. Importantly, our experiments show that the nonlinear interaction length with light for 2D TMDCs could be dramatically increased through integration with waveguides, and even achieve exact phase matching of $\chi^{(2)}$ parametric processes in a silicon photonics platform. Our results pave the way for practical $\chi^{(2)}$ nonlinear applications in silicon, including efficient wavelength conversion, parametric amplification and generation of entangled photons.

### 5.2 Waveguide design and sample fabrication

The concept behind the integration of MoSe$_2$ on a Si waveguide is illustrated in Fig. 5.2(a) (side view). A grating inscribed onto the waveguide is used to couple light from free space into the waveguide. The evanescent field of the waveguide mode at the fundamental frequency (FF) at $\sim$ 1550 nm overlaps with the MoSe$_2$ material on top of the waveguide to generate second harmonic (SH) wave. The generated SH can be guided and extracted out of the waveguide into free space by another grating coupler. Importantly, this scheme can also promote other $\chi^{(2)}$ nonlinear processes, including parametric...
amplification and spontaneous parametric down conversion (SPDC).

Slab waveguide was used in our experiments because it allows us to test the SHG at different propagation directions with respect to the TMDCs crystalline orientation. Compared to crystalline silicon whose absorption start to increase sharply below 1100 nm, hydrogenated amorphous silicon is transparent up to 700 nm owing to high optical bandgap of 1.73 eV [196]. Hence the amorphous silicon was chosen in this work because of its low optical loss at both spectral regions around 1550 nm (FF) and 775 nm (SH). The thickness of 220 nm was chosen because it was commonly used in silicon photonics platform [234, 235]. Furthermore, the TE$_0$ mode of the FF exhibits relatively strong evanescent field on the surface of the waveguide. In experiments, a 220 nm layer of hydrogenated amorphous silicon was deposited on SiO$_2$/Si wafer by plasma enhanced vapor deposition at 300 °C. The refractive index and extinction coefficient of the material was measured by ellipsometry methods afterwards.

To design the grating couplers for the FF and the SH fields, we compute the effective refractive indices of TE$_0$ FF mode and TE$_1$ SH mode. For simplicity, we use a conventional binary grating design, as schematically shown in Fig. 5.2(b) (upper part). A scanning electron microscopy (SEM) of the top view of the grating is shown in Fig. 5.2(b) (lower part) as well. In general, the coupling efficiency of the grating depends on a number of parameters, including the incident beam profile, incident angle, grating geometry, grating period, duty cycle and etching depth [131]. In our work, but without loss of generality, we implemented a grating with 50% duty cycle and a period which enables the in/out-coupling at normal incidence for the first diffraction order [131]. We experimentally tested a set of etching depths and achieved coupling efficiency of about 16%, which is reasonably good for our purpose and comparable to other couplers reported in literature [236, 237]. In order to enable multiple angles of excitation with respect to the MoSe$_2$ crystal as well as to achieve optimal coupling into the waveguide, we use a circular geometry for the grating coupler [238], where one half of the grating is designed for in-coupling of light at a wavelength of 1550 nm, while the other half out-couples light at 775 nm. The grating structure was patterned by electron beam lithography at 20 kV using the positive resist ZEP-520A. The development was performed by inserting the sample into n-Amry acetate. The resulting resist pattern was used as an etch mask for amorphous silicon etching in CHF$_3$/SF$_6$ plasma. The residual resist was removed by oxygen plasma. Details of the fabrication are shown in Fig. A.1. The optical image of the top view of the grating is shown in Fig. 5.2(c)(left).

Next, a monolayer of MoSe$_2$ is exfoliated from a bulk crystal and drily transferred onto the planar waveguide area inside the circular grating. Because the optical contrast between the monolayer and the amorphous silicon is relatively poor, we used PL mapping instead of optical microscopy to locate the MoSe$_2$ position. Figure 5.2(c) (right) shows the 2D PL mapping image of
the sample: the monolayer MoSe$_2$ crystal is the bright piece inside the grating circle. To confirm that the transferred piece is indeed a monolayer, we measured its PL emission spectrum. Figure 5.2(d) shows the PL spectrum from the location marked with a blue dot, as indicated in panel c. The spectral peak is around 1.6 eV, which agrees well with literature reports [167, 176, 193]. The micro-PL spectroscopy and micro-PL spatial mapping were performed on a commercial WiTec alpha300S system in confocal microscope configuration as shown in Fig. A.3 using excitation by 532 nm CW laser.

5.3 SHG characterization

Figure 5.3: Experimental setup for SHG characterization. Polarizer P1 and half waveplate $\lambda/2$ are used to tune the polarization of the excitation. Polarizer P2 is used to measure different components of the signal. $\lambda/2$ and P2 are mounted in automatic rotational stage so that we could measure the co-polarized component distribution. M1, M2 and M3 are removable mirrors. M1 switches between white light illumination and laser excitation, white light is used to locate the sample. M2 switches between infrared camera and CCD imaging. The infrared camera is used to locate the laser spot. M3 switches between spectral measurements and CCD imaging. Lens L1, L2 and L3 are used to condense light. DM refers to dichroic mirror, which transmits in the infrared range and reflects in the visible. Ob is objective. F is a bandpass filter. Spectro refers to spectrometer.

In the next step, we study the SHG from the MoSe$_2$ monolayer. For SHG measurements, a FemtoFiber Pro femtosecond laser of central wavelength 1550 nm, repetition rate of 80 MHz and pulse duration of 82 fs was used to pump the sample. An in-house setup was built for these measurements, the setup is shown in Fig. 5.3. Unless otherwise specified, average power of 20 mW was used. An in-house microscopy system with 20× objective was used for excitation and collection. The focused laser spot size was 5µm, the peak power density was around 15 GW/cm$^2$. In the polarization resolved measurements, a half waveplate was used to rotate the incident light polarization and another polarizer was used for detection. As discussed previously, the process of SHG is strongly enhanced by resonant pumping, near
Figure 5.4: Nonlinear SHG microscopy. (a) Emission spectra measured from the sample when focusing the pump-laser on the grating (red) and on the MoSe$_2$ (blue), the focusing positions are shown as red and blue spots in Fig. 5.2(c), respectively. (b and c) Power dependence (in log-log scale) of the peaks R1 (b) and R2 (c) as indicated in panel a. The values are normalized to the quantities obtained at 2.9 mW of FF power. The dots are the measured data and the line shows the expected quadratic dependence. (d) The polar intensity distribution of the emission component polarized parallel to the FF polarization, when rotating the pump polarization, $\varphi$, by 360$^\circ$ for both SH signal (asterisk and dashed red fitting line) and 2P-PL (black dots), the 30$^\circ$-210$^\circ$ direction corresponds to the armchair axis of the monolayer MoSe$_2$, shown schematically in the right-hand side.

The two-photon transition [58]. This justifies our material choice of MoSe$_2$, which exciton transition is resonantly matched to the two-photon energy of our pump-laser (around 0.8 eV). Under excitation by the focused FF beam, we observe strong exciton emission at 1.6 eV. The grating size in the radial direction of our sample is 10 $\mu$m and the focused laser spot is roughly 4 $\mu$m, hence we could choose to focus the laser spot either directly on the monolayer MoSe$_2$ or on the grating area. Figure 5.4(a) shows the spectra (normalized to maximum value) collected from the sample when exciting the MoSe$_2$ crystal directly from free space [blue spot in Fig. 5.2(c)] and from the waveguide through the grating coupler [red spot in Fig. 5.2(c)]. Here the spectral signal only comes from the monolayer MoSe$_2$, as we did not observe any measurable signal from waveguide region without MoSe$_2$ using a separate reference sample. Importantly, we observed approximately 5 times enhancement of the emission signal at 1.6 eV, when exciting the monolayer by the evanescent waveguide mode, as compared to excitation from free space.

We found that the signal intensity does not depend on the laser polariza-
5.3 SHG characterization

When focusing on the MoSe$_2$ directly from free space. However, when focusing on the grating, the signal intensity is heavily dependent on laser polarization, as expected for the properties of our grating coupler. The spectral data shown here has been taken by optimizing the polarization for the red spot, which corresponds to position with nearly maximum interaction length in our system.

Because the pump-laser is in resonance with the exciton energy, the SH emission and two-photon luminescence (2P-PL) are nearly degenerate. However, we still observe two peaks when focusing the laser on MoSe$_2$ directly [R1 and R2 in Fig. 5.4(a)]. There is also a broad tail in the emission spectrum when focusing on the grating. This is likely caused by the fact that the laser we used in experiments is relatively broadband (from 0.79 eV to 0.81 eV). While the signal–R1 dominates the emission, we find that both peaks scale quadratically with excitation power, as shown in Fig. 5.4(b) and (c), respectively. To further distinguish them, we measured how the different emission components depend on the polarization of the pump-laser coupled from free space. Figure 5.4(d) shows the polar distribution of the emission intensity parallel to the incident laser polarization (co-polarized component) as a function of the polarization of the excitation laser. We observe a six-fold pattern for the main peak R1 (asterisk and red dashed line), which is expected for SH signal in a monolayer TMDCs and reflects the 3-fold rotational symmetry of the crystal. From these SH microscopy measurements, we can also determine the crystalline orientation of the monolayer MoSe$_2$. This is schematically depicted on the right-hand side of Fig. 5.4(d). In contrast, the intensity of co-polarized component of peak R2, shown as black dots in Fig. 5.4(d), does not depend on the pump-laser polarization. These polarization measurements confirm that the resonant peak R1 is indeed the SH signal, while other peaks with much weaker intensity are 2P-PL. In the following discussion, we will focus only on the SH signal.

As mentioned above, the grating coupler is sensitive to the incident laser polarization and works best for TE$_0$ mode coupling, namely, when the laser is polarized along the azimuthal direction of the circular grating. The case of 2D material on top of a waveguide under TE$_0$ excitation was first studied theoretically by Haus and Reider some forty years ago and recent predictions have shown that such geometry can lead to strong SHG enhancement. However no experimental testing of these ideas have been attempted to date. Here, we measure the SH signal as a result of such interaction. To demonstrate this in details, two typical points P1 and P2 have been excited on the grating, as shown in Fig. 5.5(a) (left). The coordinate system is the same as in Fig. 5.4(d). P2 is on the armchair axis and P1 is at an angle of around 30° to it. Figure 5.5(a) (right) shows the positions of P1 and P2 relative to the coordinate system and MoSe$_2$ orientation. Firstly, we measure the overall SH intensity dependence on the polarization of the pump-laser over 360°, as shown in Fig. 5.5(b) (i, ii) for P1 and P2, respectively. The coordinates system is the same as in panel a and the angle corresponds to the polarization of the
Enhanced Second-harmonic Generation (SHG) from 2D WSe$_2$ in guided-wave geometry

Figure 5.5: SHG from MoSe$_2$ loaded Si waveguide. (a) Map of the sample orientation relative to the polar coordinate system for the measured sample (left) and schematic view (right), the armchair of the MoSe$_2$ is around 30$^\circ$ to the horizontal axis. The two spots P1 and P2 are the different positions of the laser focus on the grating, when exciting the waveguide mode. (b) Total SH emission intensity dependence on the pump-laser polarization, when focusing on position P1 (i) and P2 (ii), respectively. Co-polarized SH intensity dependence on pump-laser polarization for P1 (iii) and P2 (iv), respectively. All the intensities are normalized to the maximum value; the blue asterisks are the measured data and the dashed red lines are best fits; the angle refers to the polarization direction of the pump-laser. (c) Microscope images of the SH emission when pumping from P1 and P2, respectively, demonstrating the waveguiding and out-coupling of the SH signal.

pump-laser. We could see from these two images that both dependencies display a figure-of-eight shape distribution. This shape is entirely defined by the coupling characteristic of the grating, since the in-coupling is efficient only for one polarization.

However, the polarization dependence changes when we measure the SH emission co-polarized to the pump-laser, when varying laser polarization. The results are shown in Fig. 5.5(b) (iii, iv) for P1 and P2 excitation, respectively. We observed different profiles for these two positions, which is likely due to the combined effects from the grating coupler and the 3-fold rotational symmetry of the monolayer MoSe$_2$. Furthermore, we took snapshots of the emission when pumping at these two points as shown in Fig. 5.5(c). Bandpass filters have been applied to make sure that the signal captured by camera is dominated by the SH signal. We could see that SH signal is generated at the position of the MoSe$_2$ monolayer and is guided into the waveguide, being subsequently coupled out from the grating on the left. We note that some emission also comes back from the input end and some signal is scattered out directly from the material into free space. Importantly, the out-coupling signal was stronger when pumping from P1 compared with P2. Based on these results, we could see some hints that phase matching between TE$_0$ mode for pumping and TE$_1$ mode for SHG plays a role here, however they also indicate that multiple nonlinear wave-mixing processes exist in our system.
5.4 Theoretical calculation

Figure 5.6: Numerical simulations. (a) Effective mode indices as a function of the core thickness for the TE- and TM-polarized guided modes at the fundamental frequency (FF) and second harmonic (SH). The three red circles indicate the closest phase matching points. (b) Color scale representation of the SH conversion efficiency (on a logarithmic scale) provided by the waveguide for the three dominant three-wave-mixing processes, i.e., $\text{TE}_0 \rightarrow \text{TE}_1$ (red solid box), $\text{TE}_0 \rightarrow \text{TM}_0$ (blue dashed box) and $\text{TE}_0 \rightarrow \text{TM}_1$ (green dashed box); the radial coordinate is the waveguide length (from 0 to 30 $\mu$m) and the azimuthal coordinate is the angle between the guided-modes propagation direction and the horizontal axis. The light-blue dotted circles refers to a waveguide length of 22 $\mu$m, approximately equal to the sample size. Purple and green dots correspond to the points P1 and P2 of the experiment, respectively. (c) Total (solid red lines) and co-polarized (dashed red lines) SH intensities as functions of the pump-laser polarization angle, $\varphi$ (measured with respect to $x$-axis) when focusing on positions P1 (purple dots) and P2 (green dots).

To support our experimental results and explore further direction to optimize our system, we performed simulations based on coupled-mode theory [240]. The intensity of the SH signal depends on several factors, namely: the overlap integral between the FF and SH guided modes, the phase matching between these modes, the crystal orientation defined by the guided-modes...
wavevector and the armchair direction of the MoSe$_2$ crystal, the efficiency of the input grating for the pump-laser beam and the efficiency of the output grating in the extraction of SH light. In Fig. 5.6(a) we plot the effective mode index as a function of the waveguide thickness for the guided modes involved in SHG, assuming 1550 nm as the pump-laser wavelength.

The waveguide supports three phase matching points for SHG [red circles in Fig. 5.6(a)], involving three different combinations of guided modes at the FF and SH frequencies. The silicon core thickness (220 nm) is close to two of these points: one is associated with the TE$_0 \rightarrow$ TE$_1$ SHG process while the other is related to the TM$_0 \rightarrow$ TM$_1$ process. Our simulations suggest that the structure of the input grating, which mainly couples FF light into the TE$_0$ guided mode, favors the TE$_0 \rightarrow$ TE$_1$ interaction. In addition to this process, the nonlinear monolayer allows two other interactions originated from the FF TE$_0$ mode, i.e., the TE$_0 \rightarrow$ TM$_0$ and the TE$_0 \rightarrow$ TM$_1$. This shows the flexibility of our hybrid-integration scheme for selecting different parametric interactions, including other three-wave mixing process such us parametric amplification and generation, as well as SPDC.

The internal conversion efficiency provided by the waveguide for the dominant nonlinear interaction, TE$_0 \rightarrow$ TE$_1$, is given by

$$\eta_{TE_0 \rightarrow TE_1} = \frac{P_{SH}}{P_{FF}^2} = \xi_{NL}^2 L_{wg} \frac{\sin^2 (\Delta \beta L_{wg}/2)}{L_{wg}}$$

(5.1)

where $P_{FF}$ is the power per unit length of the FF TE$_0$ mode at the waveguide input, $P_{SH}$ is the SH power per unit length in the TE$_1$ mode measured at the waveguide output, $L_{wg}$ is the interaction length along the waveguide, $\Delta \beta = 2\beta_{FF} - \beta_{SH}$ is the wavevector mismatch. The nonlinear overlap factor in Equation (5.1) is defined as

$$\xi_{NL} = \chi_{MoSe_2}^s \sin (3\theta) \left( \frac{8\pi^2}{\epsilon_0 c \lambda_{FF}^2 n_{FF} n_{SH}^2} \right)^{1/2} \left( \frac{E_{SH}^{*(TE_1)} E_{FF}^{*(TE_0)}}{E_{FT}^{*(TE_0)} E_{SH}^{*(TE_0)}} \right) \left( \frac{\int_{z=z_{2D}} |E_{FF}^{*(TE_0)}|^2 dz}{\int_{z=z_{2D}} |E_{SH}^{*(TE_1)}|^2 dz} \right)^{1/2}$$

(5.2)

where $\chi_{MoSe_2}^s = 5.85 \times 10^{-18}$ m$^2$/V, similar to other 2D crystals (WS$_2$) [225], is the quadratic nonlinear susceptibility of MoSe$_2$, $\theta$ is the angle formed by the guided-modes wavevector and the armchair direction of the MoSe$_2$ crystal, $\lambda_{FF} = 1550$ nm is the pump wavelength, $n_{FF,SH}$ are the effective refractive indices of the FF and SH modes, $E_{FF}$ is the FF TE$_0$ mode profile and $E_{SH}$ is the SH TE$_1$ mode profile. In addition, $z_{2D}$ indicates the vertical position of the MoSe$_2$ surface, i.e., the interface between the silicon film and the air superstrate. The two normalization integrals at the denominator are calculated along the vertical direction ($z$ axis). The expressions of the efficiency and the nonlinear overlap factor for the TE$_0 \rightarrow$ TM$_0$ and the TE$_0 \rightarrow$ TM$_1$ interactions can be written in a form analogous to Equations (5.1) and (5.2) by considering
the appropriate effective refractive indices and mode profiles, and replacing \( \sin(3\vartheta) \) with \( \cos(3\vartheta) \) in order to properly take into account the 2D crystal anisotropy.

In Fig. 5.6(b) we show the calculated conversion efficiency for the three SHG processes discussed above as a function of the interaction length \( L_{\text{wg}} \) (varying from 0 to 30 \( \mu\text{m} \)) and the angle between the guided-modes wave vector and the horizontal axis. The color maps are on a logarithmic scale. The most coherent and efficient process is the \( \text{TE}_0 \rightarrow \text{TE}_1 \) interaction, whose maximum efficiency is about two orders of magnitudes larger than the efficiency of the other two processes. Due to the crystal anisotropy, when the FF \( \text{TE}_0 \) guided mode is excited near the point P1 (purple dots, corresponding to an interaction length of about 22 \( \mu\text{m} \) and \( \vartheta = 30^\circ \)), the SHG is dominated by the \( \text{TE}_0 \rightarrow \text{TE}_1 \) interaction and the other two interactions involving TM modes at the SH frequency are vanishing. On the other hand, when the \( \text{TE}_0 \) FF guided mode is excited near the point P2 of the sample (green dots, corresponding to an interaction length of about 22 \( \mu\text{m} \) and \( \vartheta = 0 \)), the opposite response is obtained, i.e., the \( \text{TE}_0 \rightarrow \text{TE}_1 \) interaction is significantly suppressed whereas \( \text{TE}_0 \rightarrow \text{TM}_0 \) and \( \text{TE}_0 \rightarrow \text{TM}_1 \) interactions are maximized.

Next, we estimate the SH light intensity at the output grating as a function of the pump beam polarization angle, \( \varphi \) and compare these theoretical results to our experimental findings. The total SH intensity extracted by the output grating

\[
I_{\text{TOT}}(\varphi) \propto \frac{1}{\Delta\vartheta\Delta\lambda} \int \int [K_{\text{TE}_1} \eta_{\text{TE}_0 \rightarrow \text{TE}_1}(\vartheta, \lambda_{\text{FF}})] \sin^2(\varphi + \Theta) d\vartheta d\lambda
+ \frac{1}{\Delta\vartheta\Delta\lambda} \int \int [K_{\text{TM}_0} \eta_{\text{TE}_0 \rightarrow \text{TM}_0}(\vartheta, \lambda_{\text{FF}}) + K_{\text{TM}_1} \eta_{\text{TE}_0 \rightarrow \text{TM}_1}(\vartheta, \lambda_{\text{FF}})] \sin^2(\varphi + \Theta) d\vartheta d\lambda
\]

(5.3)

and the portion of the SH light co-polarized with the pump laser polarization,

\[
I_{\text{CP}}(\varphi) \propto \frac{1}{\Delta\vartheta\Delta\lambda} \int \int K_{\text{TE}_1} \eta_{\text{TE}_0 \rightarrow \text{TE}_1}(\vartheta, \lambda_{\text{FF}}) \sin^2(\varphi + \Theta) \sin^2(\varphi + \Theta - \vartheta_s) d\vartheta d\lambda
+ \frac{1}{\Delta\vartheta\Delta\lambda} \int \int \left[ \cos^2(\varphi + \Theta) K_{\text{TM}_0} \eta_{\text{TE}_0 \rightarrow \text{TM}_0}(\vartheta, \lambda_{\text{FF}}) \right] \sin^2(\varphi + \Theta - \vartheta_s) d\vartheta d\lambda
+ \frac{1}{\Delta\vartheta\Delta\lambda} \int \int \left[ \cos^2(\varphi + \Theta) K_{\text{TM}_1} \eta_{\text{TE}_0 \rightarrow \text{TM}_1}(\vartheta, \lambda_{\text{FF}}) \right] \sin^2(\varphi + \Theta - \vartheta_s) d\vartheta d\lambda
\]

(5.4)

are proportional to the internal conversion efficiencies provided by the waveguide for each SHG interaction (\( \eta \) terms) and to the coupling efficiencies of the
output grating for each SH guided mode (K terms). $\vartheta$ is the angle formed by the guided-modes wavevector and the armchair direction of the MoSe$_2$ crystal. The angle $\Theta = \vartheta - \vartheta_c$, where $\vartheta_c = 30^\circ$, indicates the azimuthal position of the sample spot illuminated by the pump laser. Given its circular shape, we assume that when the input grating is illuminated by the pump laser beam, it creates a small cone of propagating guided TE$_0$ modes that originates from points P1 and P2 with angular divergence $\Delta \vartheta = 3^\circ$. In other words, $\Theta$ varies from -1.5$^\circ$ to +1.5$^\circ$ for point P1, whereas for point P2 $\Theta$ varies from 26.5$^\circ$ to +29.5$^\circ$. The double integrals in Equations 5.3 and 5.4 represent averages across the angular range $\Delta \vartheta$ and across a range of wavelengths $\Delta \lambda = 15$ nm that corresponds to the pump laser bandwidth centered around the central wavelength (1550 nm). The extraction efficiencies of the output grating for the three SH guided modes, corresponding to the coefficients $K$ in Equations 5.3 and 5.4 have been numerically retrieved with a finite-element solver (COMSOL): in particular we find that $K_{TM1} = 4K_{TE1}$ and that $K_{TM0} = 4.48K_{TE1}$. Moreover, we assume that the angular shift $\vartheta_s$ between the output polarizer, which is used to filter co-polarized SH light, and the input polarizer be equal to $4^\circ$.

The estimated total and co-polarized SH light intensities versus pump-laser polarization angle are reported in the polar plots of Fig. 5.6(c) for the two illumination positions investigated experimentally. The good agreement between theory and experiment, revealed by comparing Fig. 5.6(c) and Figures 5.5b, corroborates the idea that the waveguide is indeed boosting the SHG of the nonlinear monolayer via the three nonlinear interactions mentioned above.

Finally, we have calculated the possible maximal possible yield of SHG that the MoSe2-loaded silicon waveguide configuration could achieve under perfect phase-matching conditions. For example, the optimization of the TE$_0$ $\rightarrow$ TE$_1$ process can be obtained via complete phase matching by changing the waveguide core thickness to 236 nm. Under the pumping conditions of the experiment-spot size with a diameter of around 5 $\mu$m - and assuming diffraction-free propagation of the guided modes in the lateral (non-confined) dimension, a 22 $\mu$m long waveguide would provide a SH signal 280-times stronger with respect to the case of direct pumping of the monolayer from the top at normal incidence, i.e. in the absence of guided modes. This SH enhancement can be explained as follows: on one hand, the waveguide configuration amplifies the nonlinear interaction length by a factor $L_{wg}/t_{MoSe2}$, where $t_{MoSe2} = 0.65$ nm is the monolayer thickness; on the other hand, the overlap integral is limited by the very small thickness of the nonlinear material. It is worth stressing that, at phase matching, the enhancement factor would scale up quadratically with the nonlinear interaction length: for example, a 1-mm-long waveguide would boost the enhancement factor from 280 to 5.8x10$^5$. 
5.5 Conclusion

In conclusion, we have demonstrated the integration of TMDC monolayer on a silicon photonic platform for quadratic nonlinear optics applications. In particular, we demonstrate 5 times enhancement of SHG from atomically thin monolayer MoSe$_2$ by excitation of the 2D material by the evanescent field of the guided mode of a 220 nm planar waveguide. This enhancement is due to the increased interaction length, which proves that the nonlinear interaction length with light of 2D TMDCs, limited by monolayer thickness could be overcome by integration with waveguide. Moreover, our calculations reveal how the mode conversion works in our system in different situations and the results match well our experiments. The developed modeling predicts that the nonlinear signal could be further enhanced by optimizing the waveguide thickness to enable full phase matching condition. The results pave the way for many other nonlinear applications of 2D materials in optical domain, including parametric oscillations or efficient generation of entangled photon sources by SPDC. All such applications can be further advanced by possible electrical control of the nonlinear interactions in TMDCs [114].

Statement


In this work, HC led the projects in sample preparation, SHG characterization, data analysis, paper writing. The simulation was done with the help of MAV, DdC, CDA. All other authors contributed to some part of the projects and the discussion.
Enhanced Second-harmonic Generation (SHG) from 2D WSe$_2$ in guided-wave geometry
Conclusion and outlook

6.1 Conclusion

The renaissance of 2D materials including TMDCs has brought countless new opportunities in the ‘flatland’, in both fundamental and applied physics. In particular, the monolayer TMDCs with direct bandgap have versatile light-emitting properties including strong PL, single-photon emission, valley polarization and SHG, which makes them potentially serve for multi-functional light source in future optoelectronics. What’s more, the layered TMDCs are held together by out-of-plane van-der-Waals forces and can be transferred onto a silicon substrate without lattice-mismatch issues, which makes them suitable candidates to integrate into silicon photonics platforms.

However, challenges remain for the practical applications of monolayer TMDCs. Due to the subnanometer thickness nature of these materials, the light emission efficiency is much lower compared to other III-IV direct bandgap materials. Besides, other emission properties of 2D TMDCs such as directionality need to be well controlled for certain applications. Coupling to photonic nanostructures is promising to boost the light-emitting efficiency for these 2D materials, since photonic nanostructures have great advantages in controlling light-matter interaction at nanoscale. In this thesis, we explore integration of monolayer TMDCs into different photonic platform including metallic plasmonic and non-metallic silicon structures, and demonstrate flexible control of the emission from monolayer TMDCs, which paves the way for many applications for these 2D materials. Here is a brief summary of the work we have done.

We demonstrate integration of monolayer MoSe$_2$ onto plasmonic antenna consisting of gold bars. The plasmonic resonance is designed to overlap with PL peak from monolayer MoSe$_2$. We realize PL manipulation from strong enhancement to quenching by changing the spacer thickness between the antenna and monolayer MoSe$_2$ experimentally, and we also show control of the emission polarization to some extend. Furthermore, we investigate the coupling mechanism between the plasmonic antenna and the monolayer MoSe$_2$
Conclusion and outlook

We find that the overall quantum efficiency of the system is the main factor that affects the PL harvesting, which depends heavily on the distance between plasmonic antenna and the emitting layer. Thus, we learn that it is crucial to control the distance between the antenna and the monolayer MoSe$_2$ carefully to best harvest the PL emission. By the time we published our work, it was the first time that a plasmonic-MoSe$_2$ was studied. Importantly, we found the crucial factor that affects the coupling between the plasmonic antenna and the monolayer MoSe$_2$, which clarifies some conflicts shown in previous studies. This work paves the way for understanding the coupling between monolayer TMDCs and plasmonic platforms, thus for related applications.

We demonstrate the integration of monolayer WSe$_2$ onto silicon-based grating-waveguide scheme and realize enhanced and directional emission from monolayer WSe$_2$. By aligning the resonant modes supported by the grating-waveguide structure with both the excitation and emission wavelength, we realize average PL enhancement up to 8 times through combining both excitation and emission enhancement. What’s more, the dispersion of the modes routes the emission into defined directions, which is also polarization dependent. Thus, we realize enhanced and directional emission from monolayer WSe$_2$ by integrating with silicon-based photonic structure. In addition, we demonstrate that this grating-waveguide structure could effectively reduce the radiative lifetime of the emission from monolayer WSe$_2$, which offers the feasibility for ultrafast signal processing. Though plasmonic platform shows great advantages in confining energy at nanometer scale and thus could boost light-matter interaction dramatically, while the enhancement relies on local ‘hot’ spots. Besides, the metallic structure is not suitable for the modern silicon-photonics platform and requires precise positioning skills. In contrast, the scheme we demonstrate here is fully scalable and suitable for silicon photonics applications. This work opens the door to implement atomic-scale, multi-functional, flexible and efficient light source onto silicon photonics platform.

We propose a TMDCs-nanoantenna system that could effectively enhance and separate emission from different valleys in monolayer TMDCs into distinct directions. By mimicking the emission from valleys in monolayer WSe$_2$ (TMDCs) as circular dipole emitters, we demonstrate that the emission from different valleys goes into opposite directions when coupling to the two-bar plasmonic nanoantenna. The directionality derives from the interference between the dipole and quadrupole modes excited in the two bars, respectively. Since the emission from valleys in 2D TMDCs could be addressed by optical excitation, we could tune the emission direction from the TMDCs-nanoantenna system by tuning the pumping without changing the antenna structure. Furthermore, we discuss the general principle and further directions to improve the average performance of the nanoantenna structure. The inversion symmetry breaking and strong spin-orbit coupling in 2D TMDCs bring exciting opportunities for studying valleytronics. Especially, the emis-
sion from different valleys in monolayer TMDCs could be addressed optically, which opens new door for valley-based applications. The scheme we proposed here could potentially serve for important component for valley-based applications such as non-volatile information storage and processing.

We demonstrate enhanced SHG from monolayer MoSe\textsubscript{2} by integration with silicon waveguide. Instead of excitation from free space, we excite the monolayer MoSe\textsubscript{2} by guided modes supported by the waveguide. This scheme allows for phase matching and dramatically increases the nonlinear interaction length between the excitation light and the materials compared to free-space excitation, thus boost the second-harmonic signal. The inversion symmetry breaking in monolayer TMDCs brings new opportunities for nonlinear optics especially for SHG, while the efficiency is low due to the sub-nanometer thickness of these materials preventing them from practical applications. The scheme we demonstrate here show that the limited light-matter interaction length could be overcome by waveguide integration, thus opening lots of new opportunities for applications of these 2D TMDCs. In particular, these monolayer TMDCs are suitable for integration with silicon-photonics platform without lattice-mismatch issues, the structure we demonstrate here could serve for second-harmonic source in silicon chip, while silicon itself does not own second-order nonlinearity due to the symmetric structure. Furthermore, theoretical calculation reveals the coupling and conversion mechanisms in our system, and points out further directions for optimization. The fully scalable platform we demonstrate here brings new opportunities for these 2D TMDCs especially for nonlinear chip-integrated applications.

\section*{6.2 Outlook}

The field of 2D materials is developing rapidly, so does the new designs of photonic nanostructures. The work we demonstrate in this thesis could be extended to directions of both fundamental and applied physics, and there are plenty of exciting opportunities ahead.

More understanding of coupling between photonic nanostructures and 2D materials is needed to better control the properties of these materials. Many novel materials are emerging, for example, layered WTe\textsubscript{2} (one member of TMDCs) have been reported to possess large and non-saturating magnetoeresistance \cite{241}. Besides, new 2D materials such as boron nitride \cite{183}, phorsphore \cite{242}, and silicene \cite{243} have also been studied. On the other hand, novel photonic nanostructures especially dielectric ones \cite{187,244} with multiple types of resonances have brought unprecedented opportunities to study the coupling between the photonic structures and 2D materials. For example, it will be interesting to investigate how the resonant magnetic-type nanostructures affect the magnetoeresistance properties of WTe\textsubscript{2}. What’s more, heterostructure formed by stacking different kinds of TMDCs \cite{81,101,102}
or mixing with other 2D materials [83, 245, 246] have shown advanced electronic and optical properties, integration of these heterostructure with photonic nanostructures will further control and enhance their performance. For example, it will be intriguing to see how resonant photonic structure affects the charge transfer between different materials across the layers. What’s more, the properties of 2D materials could be tuned by electric or magnetic field, it will be interesting to investigate the tunability for hybrid structures consisting of 2D materials and photonic nanostructures. In particular, polariton modes formed through coupling between the TMDCs and cavities (strong coupling) has shown lots of interesting physical phenomena recently [247–250], there will be plenty of room to explore here.

Integration of photonic structures with devices consisting of 2D materials. Optoelectronic devices consisting of 2D materials such as photodetectors, transistors and modulators have shown excellent performance. The performances could be further improved by incorporating proper photonic nanostructures, for example, previous work has shown that the sensitivity of the photodetectors could be improved by incorporating plasmonic structures [251–255]. In addition, as we discussed, 2D TMDCs could be serve for versatile light source for future optoelectronic applications, integration of photonic structures could effectively increase the emission efficiency and the directionality. Recent work has demonstrated enhanced single-photon emission from 2D materials by integration with nanostructures [256, 257]. On the other hand, nanostructured 2D materials themselves might be used to improve the performance of devices too [184, 258], we could potentially construct hybrid system consisting of photonic structure and structured nanomaterials with the developing of materials fabrication techniques.

With the study of basic properties of various 2D materials and devices built from them, Feynman’s dream has come true. Integration of 2D material with photonic nanostructures plays an important role and drives the dream further. Looking ahead, integration of various 2D circuit elements such as TMDCs show potential to create ultra-compact, low-power, flexible electronic devices, which will revolutionize optoelectronics.
A.1 Fabrication procedures for a-Si grating

In Chapter 3 and 5 the grating are fabricated by electron beam lithography (EBL) followed by inductively coupled plasma (ICP) etching. The key step-to-step procedures are shown in Fig. A.1. In Chapter 5 the amorphous silicon layer was deposited onto a SiO$_2$/Si wafer, in the diagram of procedures, we omit the Si handle wafer. The detailed fabrication steps are laid out as below:

1. Depositing amorphous silicon (a-Si) onto glass by plasma-enhanced chemical vapor deposition (PECVD) using Oxford Instrument. The gases flow are 475 sccm Helium and 25 sccm Silane at 250 degree Celsius, chamber pressure is 1500 mTorr, the forward power is 15 W.

2. Cleaning the a-Si surface with oxygen plasma (1 min, 200 W). Spin-coating a thin layer of HMDS (hexamethyldisilazane) as an adhesion promoter (3000 rpm, 30 s) followed by a layer of diluted positive photoresist ZEP520A (6000 rpm, 2 min). Then the sample is baked for 3 mins at 180 °C. Here we do not show the layer of HMDS in the diagram.
3. Just before loading sample for EBL, a thin layer of e-spacer is coated by spin coating for conduction purpose. The grating is then patterned by electron-beam exposure (20 kV, 10 µm aperture).

4. After exposure, the e-spacer is washed away by drilled water, then cold development is performed by inserting the sample into Zep developer for 80 s followed by rinsing sample with isopropanol. The resulting photoresist patterns act as etching mask.

5. Inductively coupled plasma (ICP) etching process (15 mTorr chamber pressure, 15 W RF power, 400 W induction power) using CHF$_3$ (50 sccm) and HF$_6$ (1.8 sccm) as etch gases is conducted for form the desired structures. The etching depth is controlled via in-situ optical monitoring. The remaining photoresist is removed by oxygen plasma.

Please note that parameters such as the time duration and temperature for each process vary slightly depending on the resist and developer used for a particular sample. The numbers given here provide a rough indication of the time scale and temperature range for each process.

A.2 Transmittance characterization setup

All the transmittance data of the samples presented in this thesis are measured from the pre-existing setup shown in Fig. A.2. A halogen bulb is used as light source, whose brightness could be adjust by changing the voltage. Lens L1 with short focal length near the light source, followed by an open iris along the light path. A polarizer P1 in the light path is used to choose the polarization of incident light when linearly polarized beam is needed, which could be removed when not needed. Objective (Ob1) with a almost closed iris are used to focus light onto the sample, the iris restricts the angles of light incident into the objective (on the sample). Another objective (Ob2) in confocal configuration with Ob1 is used to collect the transmitted light. The sample is mounted onto a 3D translational stage, so we could locate our sample at the focal plane of the objectives. Light coming out of Ob2 then goes through a pair of lens (L2 and L3), between which there is an rectangular knife edge. The knife edge is used to choose the desired sample area. A removable mirror indicated as dashed line after L3 is used to switch between spectral measurements and imaging samples. when the mirror is presented in the light path, the sample is imaged on the camera through lens L4, so we could choose the desired sample region through moving the knife edge. The transmitted light is directed onto the spectrometer through an objective Ob3 (for focusing purpose).

All the lenses and distances between optical components are chosen such that the samples are illuminated with near-normal incident plane waves and
that a focused image can be obtained at the CCD camera. The objectives Ob1 and Ob2 were 20x Mitutoyo Plan Apo NIR infinity-corrected objectives with numerical apertures NA= 0.4 and focal lengths f = 200 mm. The objective Ob3 was a 10x objective of the same NA. The range of incident angles was reduced to ±3°C by the iris before Ob1.

All the transmittance measured from this system are obtained by referring to the transmitted light in the unpatterned area in our samples.

Figure A.2: Schematic of the setup for transmittance measurements. A halogen illuminates system as light source. L1, L2, L3 and L4 are lens with 1 inch diameter of carefully chosen focal lengths. Ob1, Ob2 and Ob3 are objectives used as light condenser. P represents polarizer. The solid black lines mean irises. The dashed line is a removable mirror. Spectro here refers to spectrometer.

A.3 PL mapping setup

The photoluminescence (PL) mapping of the samples shown in this thesis were measured by a commercial WiTec-alpha300S system in confocal microscope configuration, the setup of this system is shown in Figure A.3. The excitation light source are coupled into the system through fibers and we could change excitation source depending on requirements. This system could be run in both reflection and transmission mode (we show transmission here). The PL scanning is enabled by the piezo scanner and the avalanche photo diode (APD) is used to detect the signal. In addition, the spectrometer also enable us to measure the spectral data.
Figure A.3: Setup for PL mapping. The tunable light source supports wavelengths in wide range from 500 nm to 900 nm. The filters could also be changed to fit with different purposes.
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