ABSTRACT

YU, YILING. Engineering Light Matter Interaction of Atomically Thin Transition Metal Dichalcogenide Materials. (Under the direction of Linyou Cao.)

The study on class of atomically thin metal dimensional transition metal dichalcogenide materials (TMDC) is growing fast. The distinct electronic and optical properties of this material direct point to its application in the new generation of real atomically thin devices. Since it is relative new class of materials, a lot of fundamental physical problems which relate to the origin of its novel properties still need to be answered for this new emerging low dimensional material. In another hand, there are also many problems need to be solved regard to reaching high performance of the TMDC devices in real applications. Our focus is to study TMDC for understanding and engineering their strong light-matter interactions. This can be both fundamentally and practically important to TMDC nanophotonics.

We systematically studied two light-matter interaction processes of TMDC: absorption, reflection, transmission process and light emission process. The two processes are key for realizing TMDC photonic devices in different applications. For the light absorption process, we measured the layer dependent optical dielectric function of MoS2 films for the first time and demonstrates the dielectric function is dominated by excitonic effect rather than electronic band structure. Based on this conclusion, we further realize giant tunability of refractive index of monolayer TMDC by applying electrical gating field and revealed more complex underlying mechanisms. These two work no doubt pave a new way to realize CMOS compatible electro-photonic devices for atomically thin TMDC. For the light emission process in monolayer TMDC, we revealed the intrinsic limitation for TMDC is the strong many body effect, exciton-exciton annihilation. We derived the threshold pumping
power for population inversion for monolayer TMDC, which is the first step to making Laser. We also thoroughly investigated the effect of substrate to the light emission efficiency, which is the most important external environment factor. Get to the conclusion that substrate-defect assisted non-radiative recombination and substrate-borne moisture are dominating factor of quenching light emission efficiency to the monolayer TMDC, which we should avoid. This provides very useful guidance for designing TMDC based LED and Laser devices.
DEDICATION

To my dear parents!
BIOGRAPHY

The author, Yiling Yu was born on September 15\textsuperscript{th}, 1986 in Zhuzhou City in south part of China. She joined Sichuan University in Chengdu, China study Physics. After she received her Bachelor of Science degree in 2009, she enrolled in the doctoral program of the Physics department at North Carolina State University.
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CHAPT 1: Introduction and background

1.1 Introduction

Atomically thin two dimensional transition metal dichalcogenide materials (TMDC) has attracted lots of attention from researchers in recent years since it is discovered [1]. This monolayer TMDC family shares some similarities with graphene. They are both composed of one single atomic layer with hexagonal arrangement of atoms crystal structures. The interaction between different layers for both TMDC and graphite is only Van der Waals force, makes the surface passivated without dangling bonds.

![MX2 structure with (a) top view and (b) side view.](image)

Figure 1.1. MX2 structure with (a) top view [2] and (b) side view.

They both have strong mechanical strength that can apply to elastic devices [3, 4]. The key difference between TMDC and graphene is that the TMDC is semiconductor material however graphene is semi-metal lacking of band gap. So graphene has limited application in
functional optoelectronic devices that require good on and off switch. However for TMDC, they have band-gaps range from 1.6ev to 2.1ev depend on their composition and layer numbers[5, 6]. Though the mobility of TMDC is not as good as graphene, The TMDC still can reach to high mobility [7, 8]. All of these electronic properties make TMDC a very promising candidate that can lead to real next generation atomically thin devices era. What’s more important, the TMDC has very novel optical properties. Their band-gap is located in visible light region, and with extremely strong light-matter interaction even with single layer material due to its strong excitonic effect. It will be the main topic I will discuss in this thesis. The TMDC material can change from indirect band gap material to direct band gap material when thickness reduces to monolayer. Very high luminescence efficiency has been observed for monolayer TMDC [9, 10]. Efficient TMDC based LED has been realized [11, 12]. People even successfully make out laser based on this monolayer TMDC [13, 14]. Overall, the extraordinary optical and electronic properties of 2D TMDC make it great material to realize next generation atomically thin optoelectronic devices.

1.2 Strong excitonic effect of 2D TMDC

Excitons are coupled electron-hole pairs via coulomb attraction. The distinct optical properties of 2D TMDC are originating from the strong excitonic effect of the material. Since it is atomically thin layered materials with very small Bohr radius, so the dielectric screening effect for exciton is very small. It leads to very large exciton binding energy. The simplified picture of exciton in monolayer is illustrated in Fig 1.2.
Figure 1.2. Exciton in monolayer MX2. The interaction of electron-hole pair can go out of the material reduces the dielectric screening effect, generating strong binding energy.

For conventional bulk semiconductors or semiconductor quantum wells, the exciton binding energy is smaller than 100mev. However for monolayer TMDC such as monolayer MoS2, WS2, WSe2, their exciton binding energy are of one order higher magnitude range from 400mev to 800mev [15-21]. The strong binding energy also results in very strong many-body interactions for this low dimension material. For instance, the charged exciton called trion, which is one extra carrier bound to a neutral exciton form a three body complex, can be observed at room temperature in TMDC. But for conventional semiconductors, trion can only observed at low temperature region. I will show later in the thesis that this trion has profound effect on the optical properties of 2D TMDC. Moreover, not only strong three-body effect exist, even higher order interaction like exciton-exciton interaction also play very important role in the light emission efficiency of monolayer TMDC. We will also discuss this in Chapter 4. In fundamental wise, the 2D TMDC really provide a perfect platform to observing, studying the many-body interaction, which has been the most important topic in condensed matter physics. In engineering wise, the exciton involved many-body interaction can be tuned by electric field. And many-body interaction is intrinsically affected by the density of excited excitons which is determined by excitation power. These indicate possibility to control the optical properties by both electrical ways and optical ways.
This thesis will address to answer two questions: How the strong exciton many body effects affect the optical properties of 2D TMDC? How to engineering the excitonic effects to improve the optical performance of 2D TMDC?

1.3 Light-matter interaction of 2D TMDC

There are two main processes for light-matter interaction of 2D TMDCs, which are also two key processes relate to application of 2D TMDCs in photonic devices. One is the light absorption, reflection and transmission process. Another one is the light emission process. The light absorption/reflection/transmission process is dominated by the optical dielectric function of the 2D TMDCs. Even for a single layer TMDCs, it can have very strong absorption and reflection efficiency to the light.

Figure 1.3. Transferred different layer MoS2 film onto SiO2/Si substrate.

For example, the monolayer MoS2 can even be seen on the substrate [22] with high optical contrast with thickness three orders of magnitude smaller than the wavelength of incident
light. Monolayer MoS2 has been proved to have 5% solar absorption [23]. These are due to strong quantum confinement effect and weak screening effect of the excitons when the layer thickness reduces to a few atoms thickness. Fig. 1.4 shows the absorption efficiency spectrum of the single suspended MoS2 layer, it can absorb over 20% of light around 430nm (C exciton peak) and 7% of light in range 600nm to 680nm (A exciton and B exciton peaks). This makes atomically thin layer 2D TMDCs potentially a very good platform to realize functional nanophotonic devices such as ultrathin optical modulator, solar absorber and phase steering meta-surfaces.

Figure 1.4. Absorption efficiency of monolayer suspended MoS2 in visible light range.

The quantum efficiency is most important property of light emission. Enhancing the light emission efficiency is the key to use the material to realize application like LED and Laser. For the 2D TMDCs, the monolayer TMDCs are direct band gap material while the multilayer TMDCs are indirect band gap material Fig. 1.5. Only the monolayer TMDCs promised to high light emission efficiency.
Figure 1.5. Calculated band structures of (a) bulk MoS$_2$, (b) quad- rilayer MoS$_2$, (c) bilayer MoS$_2$, and (d) monolayer MoS$_2$. The solid arrows indicate the lowest energy transitions. [5]

So we will only focus our discussion on monolayer light emission. The light emission process is determined by the recombination process of excited excitons (Fig 1.6). The efficiency is determined by the competition between the radiative recombination rate and non-radiative recombination rate. To enhance the light emission efficiency is about to increase the radiative recombination rate and suppress the non-radiative recombination rate.

Figure 1.6. Illustration of exciton recombination process.
The radiative recombination rate is determined by radiative lifetime of exciton $k_r = 1/\tau_r$. Same to the non-radiative lifetime $k_{nr} = 1/\tau_{nr}$. The radiative lifetime of exciton is mostly determined by the intrinsic properties of the material that only relate with the exciton binding energy and band structure. The non-radiative lifetime however is affected by extrinsic properties, such as defects, impurities, doping level and substrate conditions.

![Exciton-exciton annihilation process](image)

**Figure 1.7.** Illustration of exciton-exciton annihilation process.

Due to the strong exciton binding energy of monolayer TMDCs, strong many-body interaction caused nonlinear higher order recombination term like exciton-exciton annihilation Fig. 1.7 will also play a very important role, which we will discuss in detail in Chapter 3.

### 1.4 Experimental methods

There are several important optical spectroscopy methods to characterize the low dimensional TMDCs. There are two categories of the optical characterize methods, one is time averaged spectroscopy and another one is time resolved spectroscopy. The time average spectroscopy methods include time average photoluminescence measurement,
reflection/transmission spectroscopy and Raman spectroscopy. These measurements have time scale much longer than the material response time, so the measurements are detecting the physical response from steady states. This kind of characterization not only tells information of fundamental properties of the material but also reveals how good is the optical performance of the material that directly relate to the device performance. In addition, the Raman spectroscopy is very useful tool to identify the layer number of TMDC which is pretty difficult for other techniques. Even atomic force microscopy sometimes cannot get precise layer number when thickness goes down to below 1nm to 2nm scale. The Raman spectroscopy essentially detects the inelastic electron-phonon scattering signal so as to show the phonon modes properties. Take MoS2 film as an example. There are two signature phonon modes in the range from 350cm$^{-1}$ to 450cm$^{-1}$. One is in plane optical phonon mode $E_{12g}$, another is out of plane mode $A_{1g}$ (Fig 1.8). As the layer number increases, the $A_{1g}$ vibration mode will be compressed that lead to blue shift of the Raman shift of $A_{1g}$ peak. Meanwhile, for the in plane $E_{12g}$ mode, increasing layer number will results in larger dielectric screening. It will soften the $E_{12g}$ vibration mode which cause redshift to $E_{12g}$. This will give us the layer dependent Raman spectrum like showing in Fig 1.8 Generally, the Raman shift difference between $A_{1g}$ and $E_{12g}$ peaks can precisely determine the layer numbers, for monolayer the difference is range from 19cm$^{-1}$ to 20cm$^{-1}$; bilayer is 22cm$^{-1}$ to 22.5cm$^{-1}$; trilayer is around 23cm$^{-1}$ and four layer is around 24cm$^{-1}$.
For the time resolved spectroscopy, this kind of measurement can resolve the physical response of the material in a very short time scale before the system reach to steady state. The time resolved spectroscopy provide perfect way to detect the dynamics of the carriers and excitons, which is very important to understand the fundamental physics process that affect the optical performance. In this thesis, the main time resolve spectroscopy technique been used is pump probe transient absorption spectroscopy. The carriers in the material have been pumped to excited states a short pulse laser (150fs) with photon energy larger than the band gap (2.1ev), and a time-delayed probe pulse beam with photon energy around the band edge (1.88ev for MoS2, 2ev for WS2 and 1.76v for WSe2) is used for detect the differential reflection ($\Delta R/R$). $\Delta R$ is the reflection difference between with pump and without pump. After the system has been pumped, the conduction (valence) band has been occupied by the excited electrons (holes), so the absorption of the probe beam will be less compare to before
pumped. That will be indicated by change in reflection also. The excited excitons will recombined after ps or ns scale, the change in reflection of probe beam would be able to tell the population of excitons in the excited states in time range from 0ps to 500ps. So the exciton dynamics information can be acquired.
CHAPT 2: Exciton dominated dielectric function of atomically thin MoS$_2$ films

We systematically measure the dielectric function of atomically thin MoS$_2$ films with different layer numbers and demonstrate that excitonic effects play a dominant role in the dielectric function when the films are less than 5-7 layers thick. The dielectric function shows an anomalous dependence on the layer number. It decreases with the layer number increasing when the films are less than 5-7 layers thick but turns to increase with the layer number for thicker films. We show that this is because the excitonic effect is very strong in the thin MoS$_2$ films and its contribution to the dielectric function may dominate over the contribution of the band structure. We also extract the value of layer-dependent exciton binding energy and Bohr radius in the films by fitting the experimental results with an intuitive model. The dominance of excitonic effects is in stark contrast with what reported at conventional materials whose dielectric functions are usually dictated by band structures. The knowledge of the dielectric function may enable capabilities to engineer the light-matter interactions of atomically thin MoS$_2$ films for the development of novel photonic devices, such as meta-surface, waveguides, light absorbers, and light emitters.

2.1 Introduction

Two-dimensional (2D) transition metal dichalcogenide (TMDC) materials have been known exhibiting strong exciton binding energy that may be one order of magnitude larger than conventional semiconductor materials[1, 25-29]. However, how the extraordinarily strong exciton binding energy could affect the light-matter interactions such as dielectric functions of the materials has remained unexplored. The lack of knowledge about the dielectric function has significantly limited the application of 2D TMDC materials in many exciting
photonic fields such as metamaterials[30], which relies on the sophisticated manipulation of effective dielectric functions to enable novel optical functionalities. In this work we have measured the dielectric function of atomically thin MoS$_2$ films and discovered that it is dominated by the effect of the tightly bound excitons, as evidenced by an anomalous dependence of the dielectric function on the layer number. The dielectric function decreases with the layer number increasing when the MoS$_2$ films are less than 5 layers thick, but turn to increase with the layer number for thicker. We also quantitatively evaluate the exciton binding energy and Bohr radius of the thin films by fitting the experimental results with an intuitive model. The observed dominance of excitonic effects in the dielectric function is in stark contrast with what expected at conventional materials, whose dielectric functions are usually dictated by band structures[31, 32]. Our success in this discovery is built upon a unique self-limiting chemical vapor deposition (CVD) process that we have recently developed[33]. The self-limiting CVD process can be used to grow centimeter-scale, uniform, and high quality atomically thin MoS$_2$ films with controlled layer numbers and remarkable uniformity (Fig. 2.1). This allows us to examine the dielectric function of MoS$_2$ films as a function of well-defined layer numbers. Our work is different from earlier research for the dielectric function of MoS$_2$ films[34, 35], whose results are likely inaccurate due to the lack of satisfactory uniformity or precise control of the layer number.

2.2 Measurement of layer-dependence of the dielectric function

We measured the dielectric function ($\varepsilon_1 + i\varepsilon_2$) of as-grown MoS$_2$ films on sapphire substrates using spectroscopic ellipsometry[36]. Fig. 2.3a-b shows the real $\varepsilon_1$ and imaginary $\varepsilon_2$ parts of
the dielectric function in the visible range that are derived from experimental measurements (see Fig2.2 for the fit between experimental and simulated results).

**Figure 2.1.** The AFM measurement of MoS2 film with different layer number. (a) 1 layer and 2 layer. (b) 3 layer and 4 layer. (c) 5 layer and 6 layer. (d) 7 layer and 8 layer.
**Figure 2.2.** The ellipsometry measurement fitted results for delta and phi of MoS2 film with different layer number. (a) 1 layer to 5 layer. (b) 6 layer and 10 layer.
Owing to the extreme geometrical anisotropy of the film, what we obtained is actually the in-plane component of the dielectric tensor because the out-of-plane dielectric function may only contribute trivially to the optical response due to the difficulty in exciting the vertical dipole of the atomically thin film[36]. As further evidence for the measured in-plane dielectric function, we performed the spectroscopic ellipsometry at different incident angles (40°-75°), and all of them ended up with giving very similar dielectric functions. The dielectric function of bulk MoS$_2$ is also measured and plotted in Fig. 2.3 as a reference, the result of which is consistent with what reported previously[37].
Figure 2.3. Anomalous layer-dependence of the dielectric function of 2D MoS$_2$. (a-b) Real and imaginary parts of the dielectric function of 2D MoS$_2$ vs. layer number. Also given is the dielectric function of bulk MoS$_2$. The three peaks can be assigned to $A$, $B$, and $C$ excitons as labeled. (c) The dependence of the imaginary part $\varepsilon_2$ of the dielectric function at the $A$, $B$, and $C$ peaks on layer number. The error bar is 5% and estimated from the measurement results of multiple samples. (d) Normalized $\varepsilon_2$ at the $A$, $B$, and $C$ peaks vs. layer number. The normalization is performed with respect to the corresponding value of each peak in the 5-layer MoS$_2$. Error bar is ignored for visual convenience.

The three peaks in the spectral dielectric function can be assigned to $A$, $B$, and $C$ from low to high energies, respectively[20, 38-40]. The $A$ and $B$ peaks are related with the transition from the spin-orbit split valence bands to the lowest conduction band at the $K$ and $K'$ points, while the $C$ peak is associated with the transition from the valence band to the conduction band at the part of the Brillouin zone between the $A$ and $\Gamma$ point[39, 40].
Figure 2.4. Independence of the measured dielectric function from synthetic processes and substrates. (a) Measured dielectric constants of as-grown monolayer MoS2 made by two different CVD processes, one using MoCl5 and S as the precursors and the other using MoO3 and S as the precursors. The growth substrate in both growths is sapphire. (b) Measured and simulated reflection spectra of monolayer MoS2 on different substrates, sapphire and silicon with 80 nm thick thermal oxide. The monolayer MoS2 involved is grown on sapphire substrates and then transferred to SiO2/Si substrates. The simulation uses the optical constant measured with the as-grown MoS2 on sapphire substrates.

The measured dielectric function is not sensitive to the synthetic process or the substrate. The dielectric functions measured from the MoS2 grown by using MoCl5 and S as the precursors[33] and by using MoO3 and S as the precursors[41] are essentially identical (Fig 2.4a). We also find that the dielectric functions of the as-grown MoS2 films on sapphire substrates and those transferred onto SiO2/Si substrates are identical (Fig 2.4b). Additionally, the dielectric function of the film is stable under ambient environment.
We monitored the dielectric function of the as-grown MoS$_2$ films on sapphire substrates as a function of the time for the films to be exposed to ambient environment. We monitored the dielectric function of the films exposed to ambient environment for more than one week and found no change in the measured result (Fig. 2.5). The result we measured for the monolayer MoS$_2$ film is consistent with what previously measured using spectroscopic ellipsometry$^{20}$ but is 10-15% less than the results derived from absorption spectra$^{[42, 43]}$. We do like to point out some difference in the spectroscopic ellipsometry used by us as well as Ref.42 and the spectroscopic absorption technique used in Ref.43. Spectroscopic ellipsometry is the most established technique for the measurement of dielectric functions, in which two parameters are measured at each wavelength and the dielectric function can be uniquely determined in any spectrum range with the thickness information of the film independently determined by AFM. The dielectric function may be derived from spectroscopic reflection using the Kramer-Kronig relationship as well. But to precisely find out the dielectric

**Figure 2.5.** Stability of the dielectric function. Real (upper panel) and imaginary (lower panel) parts of the dielectric function of monolayer MoS$_2$ measured at different times after synthesis.
function using the Kramer-Kronig relationship requires information of the absorption in the entire spectral range. In Ref.43 the absorption of the monolayer in the range higher than 3 eV, whose value is not experimentally available, is assumed to be equal to that of the bulk counterpart. This assumption might overestimate the dielectric function to some degree. We believe this is likely the reason why our result is around 10-15% less than the result reported in Ref.43.

Significantly, the measured dielectric function shows an anomalous dependence on the layer number (Fig. 2.3). It decreases with the layer number increasing when the film is less than 5-7 layers thick and then turns to increase with the layer for thicker films. We were very careful to ensure no artifact introduced in the measurement. More specifically, we performed extensive AFM for each of the films studied prior to the ellipsometry measurement and confirmed the atomic-scale smoothness (roughness usually < 0.5 nm except the 8L, 9L and 10L films, whose roughness is a little bit larger in the range of 0.7-0.9 nm, see Fig 2.1) and excellent uniformity of the film. Additionally, for the result of each layer number, we measured at least three different sets of samples and observed only minor variation (5%) in the resulting dielectric function. To further illustrate this anomalous layer-dependence, we extract the imaginary part of the dielectric functions at the A, B, and C peaks from Fig. 2.3b and plot it as a function of the layer number (Fig.2.3c). The result clearly shows a decrease and then an increase in the dielectric function with the layer number continuously increasing from one. The layer dependence is similar for all the A, B, and C peaks (Fig. 2.3d). Given the similarity in the layer dependence, we only focus on the C peak in the following discussion.
2.3 Strong excitonic effect on layer dependent dielectric function

To obtain physical insights into the observed layer dependence, we examine the dielectric function from the perspective of quantum mechanics. We only focus on the imaginary part $\varepsilon_2$ because the real part $\varepsilon_1$ can be deterministically correlated to $\varepsilon_2$ by the well-established Kramer-Kronig equation[44]. Fundamentally, $\varepsilon_2$ is related with interband transitions as[31, 44, 45]

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m_0^2 \omega^2} J_{cv} |p_{cv}|^2 \left| U(0) \right|^2 \frac{\Gamma / 2}{(E_{cv} - \hbar\omega)^2 + (\Gamma / 2)^2}$$  \hspace{1cm} (2.3.1)

where $\omega$ is the frequency, $\hbar$ is the Planck’s constant, $e$ and $m_0$ are the charge and mass of free electrons, $J_{cv}$ is the joint density of the initial (valence band) and final (conduction band) states involved in the transition. $p_{cv}$ is an optical matrix element indicating the probability of the transition from the initial to final states. It consists of an integral over a unit cell that involves the momentum operator as well as the unit cell wavefunctions in the conduction and valence bands. $|U(0)|^2$ represents the effect of excitons on the oscillator strength of the interband transition, where $U$ is the relative motion wavefunction of the eletrons and holes bound by Coulomb interactions and $\theta$ indicates the physical overlap of the electron and hole wavefunctions. $E_{cv}$ is the optical energy gap between the conduction and valence bands involved and $\Gamma$ is a damping constant determining the bandwidth of the interband transition.

For simplicity, we only focus on the dielectric function at the peak position (on-resonance) as shown in Fig. 2.3c-d, where $E_{cv} - \hbar \omega = 0$ and Eq.(2.3.1) can be simplified as

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m_0^2 \omega^2} J_{cv} |p_{cv}|^2 \left| U(0) \right|^2 \frac{2}{\Gamma}$$ \hspace{1cm} (2.3.2)
Physically, $\Gamma$ represents the width of the peak. From Fig. 1b the peak can be found phenomenally remaining to be similar in the films with different layer numbers. Therefore, it is reasonable to consider that $\Gamma$ is independent of the layer number. The optical matrix element $p_{cv}$ is also independent of the layer number because it is only related with unit cells and unit cell wavefunctions, both of which are not dependent on the layer number. The independence of $p_{cv}$ on geometrical features has previously been demonstrated at quantum wells[46]. Therefore, Eq. (2.3.2) can be further simplified as

$$\varepsilon_2(\omega) = A_0 J_{cv} |U(0)|^2$$

(2.3.3)

where $A_0$ includes all the terms independent of the layer number. Eq. (2.3.3) indicates that the layer dependence of the dielectric function may result from only two parameters: the joint density of states $J_{cv}$ and the excitonic effect $|U(0)|^2$.

![Figure 2.6. Comparison of the measured and calculated dielectric function of 2D MoS$_2$. (a) Calculated imaginary part $\varepsilon_2$ of the dielectric function of MoS$_2$ with different thickness. (b) Comparison of experimental and calculated results for $\varepsilon_2$ at the C peak as a function of the layer number. The error bar in the experimental result is ignored for visual convenience.](image)
We can get more insight by further examining the specific layer dependence of the two parameters $J_{cv}$ and $|U(0)|^2$. The joint density of states $J_{cv}$ is determined by the band structure and expected to monotonically increase with the layer number. This is because the density of states in 2D materials is well known to be smaller than that in 3D materials[31, 44] and the increase of the layer number in effect enables a continuous evolution from two dimensions (monolayers) to three dimensions (bulk). To quantitatively elucidate the layer dependence of $J_{cv}$, we calculate the $\varepsilon_2$ of MoS$_2$ films using density functional theory (DFT) techniques without considering excitonic effects[20]. The calculation result is given in Fig. 2.6a and essentially represents the density of states $J_{cv}$. It reproduces the major spectral features of the experimental results and indeed shows a monotonic increase with the layer number. For the convenience of comparison, we plot the calculated and measured dielectric functions at the $C$ peak as a function of the layer number in Fig. 2.6b. The calculated results are understandably smaller than the experimental results due to the exclusion of exciton effects. Of our interest is to compare the layer dependence in the calculated and experimental results. The similarity of the two results for the films > 5L suggests that the observed layer-dependent increase in the dielectric function in the relatively thicker films may be correlated to the effect of the density of states $J_{cv}$. However, for the films less than 5 layers thick the calculated layer-dependence is opposite to the experimental observation (Fig. 2.6b). This can be correlated to the other parameter not considered in the calculation, the excitonic effect $|U(0)|^2$. The excitonic effect is expected to be strong and to quickly decrease with the layer number due to the well known layer-dependent exponential decrease of exciton binding energy[38].
Figure 2.7. Strong, layer-dependent excitonic effects in atomically thin MoS$_2$ films. (a) The position of the $C$ peak in MoS$_2$ films as a function of the thickness of the film $L$. The error bar $\pm 0.005$ eV results from the possible errors in determining the peak position. The dashed lines are the fitting results using the model of infinite quantum wells (fitting 1) and the quantum well in fraction space (fitting 2) (b) The position of the $C$ peak in MoS$_2$ films as a function of $1/L^2$, where $L$ is the thickness of the film. The red line is the fitting results using the model of infinite quantum well with the fitting equation given as shown. The inset is a magnified version of the area indicated by the dashed yellow rectangle. (c) The dependence of the binding energy and exciton radius in MoS$_2$ films on the layer number.

The layer-dependent excitonic effect can be understood more quantitatively by examining the excitonic peak position with an intuitive model that involves quantum confinement and exciton binding energy. Of our interest is to quantitatively evaluate the layer dependence of the exciton binding energy from the observed evolution of the $C$ exciton peak position with the layer number (Fig. 2.7a). The excitonic peak position (i.e. optical bandgap) is equal to the electronic bandgap minus the exciton binding energy, and its layer dependence originates from the layer dependence of both components. Should the layer dependence of the electronic bandgap be found out, we would be able to figure out the layer dependence of the exciton binding energy from the measured excitonic peak position. It is actually very difficult
to experimentally or theoretically evaluate the electronic bandgap of MoS$_2$ with different layer numbers. However, we find out that the layer dependence of the electronic bandgap may be reasonably correlated to quantum confinement effects. The peak position of the $C$ exciton $E_C$ in the films thicker than 7 layers shows a linear dependence on $1/L^2$ (Fig. 2.7b), and can be fitted by the conventional model of infinite quantum wells as $E_C = E_g + R_y + \frac{\pi^2 \hbar^2}{2m_{\text{eff}} L^2} - R_y$. where $E_g$ is the position (optical bandgap) of the $C$ peak in bulk MoS$_2$ materials ($E_g = 2.695$ eV as measured in Fig. 2.3b), $R_y$ is the exciton binding energy and assumed not changing with the thickness in the model of infinite quantum wells, and $m_{\text{eff}}$ is the reduced electron-hole effective mass of the film. The introduction of $R_y$ in the equation is to illustrate that the optical bandgap is equal to the electronic bandgap (the first three terms) minus the exciton binding energy (the last term). The fitting to the experimental results (the red lines in Fig. 2.7a-b) gives $E_C = 2.695$ eV + 150.9/$L^2$, from which we can derive the reduced effective mass $m_{\text{eff}} = 0.250 m_0$ for the $C$ extions in bulk MoS$_2$ and the films thicker than 7 layers. We can also derive the exciton binding energy $R_y = 58.9$ meV and Bohr radius $a_b = 1.61$ nm in bulk MoS$_2$ and thick films, in which the static dielectric constant is set to be 7.6 as measured for bulk MoS$_2$ previously[47].

The peak position $E_C$ in the films thinner than 5-7 layers shows apparent deviation from the model of infinite quantum wells (Fig. 2.7b). Instead, we can fit the experimental results with a model of quantum wells in fractional dimensional space as[48, 49]

$$E_C = E_g + R_y + \frac{\pi^2 \hbar^2}{2m_{\text{eff}} L^2} \left[ \frac{(D-1)/2}{2} \right]^2 - \frac{R_y}{\left[ \frac{(D-1)/2}{2} \right]^2}$$  (2.3.4)

where $D$ is the effective dimensionality that is defined by the ratio of the exciton binding energy $R_y^*$ in the films and that of bulk MoS$_2$ $R_y$ as $\left[ \frac{(D-1)/2}{2} \right]^2 = R_y^*/R_y$. Again, the first
three terms of eq. (4) represent the electronic bandgap and the last term indicates the exciton binding energy. The factor of \( [(D-1)/2]^2 \) in the third term originates from the change in the effective mass associated with the effective dimensionality. For the films thicker than 7 layers, \( D \) is 3 and Eq. (2.3.4) is then reduced to the equation for infinite quantum wells. By fitting the experimental results with Eq. (2.3.4), we can have the effective dimensionality \( D \) as 1.75, 2.07, 2.30, 2.51, 2.65, and 2.83 for the films in layer number of 1, 2, 3, 4, 5, and 6, respectively. We can then derive the corresponding exciton binding energies using \( R_y^* = R_y/[(D-1)/2]^2 \) as 0.421 eV, 0.206 eV, 0.139 eV, 0.103 eV, 0.0865 eV, and 0.0704 eV; we can also derive the corresponding Bohr radius of excitons from \( a_b^* = a_b(D-1)/2 [48, 49] \) as 0.602 nm, 0.861 nm, 1.04 nm, 1.22 nm, 1.33 nm, and 1.47 nm, respectively. These results are plotted in Fig. 2.7c.

The model we used to fit the experimental result is based on an assumption that the layer dependence of the electronic bandgap can be ascribed to the effect of quantum confinement. This is supported by our experimental results, in particular, the consistence between the observed peak position of the films thicker than 7 layers and what predicted from the model of infinite quantum wells. However, more theoretical and experimental studies would be necessary to provide more rigorous support, which is to our best knowledge expected to very difficult. Nevertheless, the result we obtained by fitting the experimental results using this model seems to be reasonable when compared to the limited number of studies on the exciton binding energy and Bohr radius available in the literature. There is not study that would allow us to systematically crosscheck all of our results. For instance, the binding energy \( R_y = 58.9 \) meV and Bohr radius \( a_b = 1.61 \) we derived for the \( C \) exciton in bulk MoS\(_2\) and thick films is reasonably consistent with the binding energy and Bohr radius reported for the \( A \)
exciton in bulk MoS$_2$, which are 87.2 meV and 1.11 nm, respectively[50]. Additionally, the Bohr radius (0.602 nm) we derived for the C exciton in monolayer MoS$_2$ nicely matches the theoretical prediction, $\sim$ 0.5 nm[40]. The derived binding energy (0.421 eV) is reasonable compared with what reported for the A exciton, which is believed to be 0.4-0.6 eV in monolayer MoS$_2$ [20, 21].

With the information of the exciton binding energy and radius, the observed layer dependence of the dielectric function can be intuitively understood from a perspective of geometric confinement. Fig. 2.8 shows the comparison between the size of excitons and the thickness of the film. While the film is highly anisotropic, the size of the exciton is schematically illustrated by the diameter of a sphere anyway. This is because Eq. (2.3.4), which we used to derive the exciton radius, treats the excitons as spheres in an isotropic space by converting the geometrical anisotropy into fractional dimensionality[48, 49]. The size of the exciton in bulk MoS$_2$, 3.22 nm, is close to the thickness of the 5L film, 3.10 nm (Fig. 2.8a). Therefore, the exciton in MoS$_2$ films is expected to start experiencing substantial geometrical confinement when the layer number of the film is decreased to 5, which may lead to decrease in the exciton size. Intuitively, a smaller exciton radius can better facilitate the spatial overlap of the electron and hole wavefunctions and subsequently cause larger amplitude in $|U(0)|^2$. The layer-dependent decrease of the dielectric function is expected when the layer-dependent decrease of the excitonic effect offsets or even exceeds the layer-dependent increase of the joint density of states.
Figure 2.8. Geometric confinement of excitons in MoS$_2$ films. (a) Comparison of the size of the exciton in bulk MoS$_2$ with the thickness of MoS$_2$ films. The regime where the film is thinner than the exciton size is categorized as strong confinement. (b-e) Schematic illustration of the size of excitons in the films with different layer numbers.

The main conclusion we draw from the analysis of the $C$ exciton, i.e. the dominance of excitonic effects in the dielectric function, can be applied to the $A$ and $B$ excitons as well due to the similar layer dependence in corresponding dielectric functions (Fig 2.3c-d). However, it is difficult to quantitatively extract the binding energy and Bohr radius for the $A$ and $B$ excitons as what we did for the $C$ exciton. This is because that the positions of the $A$ and $B$ excitons do not show substantial layer dependence as what observed as the $C$ exciton, which makes the fitting by the intuitive model difficult. One reason for the less layer dependence observed at the $A$ and $B$ excitons could be related with the random variation of the position of the $A$ and $B$ excitons due to local doping effect from the substrate, which may be as large as $\sim$ 10 meV [51]. Another reason could be related with the better localization of the $A$ and $B$ excitons in the plane of the film, which may lead to a less dependence on interlayer interactions[22].
2.4 Conclusion

While our work mainly focuses on MoS$_2$, we believe that similar dominance of excitonic effects in the dielectric function could generally exist in all the atomically thin semiconducting TMDC materials. Our result bears significant implications for the development of photonics devices with 2D TMDC materials. The obtained dielectric function and refractive index for the MoS$_2$ with different layer numbers can be immediately useful for the rational design of photonic devices. In particular, as excitons are subject to influence of electric or magnetic fields, the dominance of excitonic effects in the dielectric function makes atomically MoS$_2$ films an unprecedented platform that may enable the development of field-effect photonics, whose optical functionalities would be tuned by external electric or magnetic fields.
We report that the refractive index of transition metal dichalcogenide (TMDC) monolayers, such as MoS$_2$, WS$_2$, and WSe$_2$, can be substantially tuned by up to 60% using CMOS-compatible electrical gating. This strong tunability is rooted in the strong excitonic effect of the monolayers and the high susceptibility of the excitons to the influence of free charge carriers. More specifically, we have elucidated that the tunability mainly results from the effects of free charge carriers on spectral broadening and the inter-transfer of transition probabilities between neutral and charged excitons, while the other effects of free charge carriers, including bandgap renormalization and change of exciton binding energy, only play negligible roles. The electrical gating of refractive index may open up a new age of field-effect photonics in which the optical functionality can be dynamically controlled in speed comparable to that of state-of-art CMOS circuits.

3.1 Introduction

Electrically gating photons in ways comparable to the gating of electrons has the potential to revolutionize the photonic industry. It would enable the development of unprecedented dynamic photonics with operation speed comparable to that of state-of-art CMOS circuits. It would also enable chip-scale integration of optical functions into electronic circuits, which could dramatically improve the computing speed [52, 53]. However, the electrical gating of photons is very challenging because of the difficulty in gating refractive index. Photon is charge neutral and cannot be directly manipulated by electric fields. The electrical control of photons may only be realized by virtue of light-matter interactions, for instance, reflection,
transmission, absorptions, and scattering. As refractive index consists of the most fundamental measure for light-matter interactions, to gate photons is in essence to gate refractive index. None of the existing approaches for electrically gating refractive index may provide satisfactory tunability, tuning spectral range, speed, and compatibility with CMOS circuits. The most common strategy to electrically tune refractive index relies on the plasma dispersion effect of free charge carriers, in which the optical absorption of injected electrons or holes may give rise to changes in the refractive index.[54-61] But the density of the charge carriers that can be injected is limited, and this fundamentally limits the tunability in refractive index, usually in the scale of 0.1-1%. [54-58] While ionic gating has been recently reported to be able to enable larger tunability,[62-64] its nonlocal nature, inferior chemical stability, and intrinsically slow switching make it not ideal in terms of speed and compatibility with CMOS circuits.

Here we demonstrate that the refractive index of monolayer transition metal dichalcogenide (TMDC) materials, including MoS$_2$, WS$_2$, and WSe$_2$, can be substantially tuned by up to 60% using CMOS-compatible gating. Unlike the previous approach of relying on the plasma dispersion effect of free charge carriers to tune the refractive index,[54-58] this large tunability in refractive index is rooted in the strong excitonic effects of the monolayers [65] and the high susceptibility of excitons to the influence of free charge carriers. More specifically, we have discovered that the tunability is mainly due to the effects of free charge carriers in spectral broadening and the inter-transfer of transition probabilities between the neutral and charged excitons, while the other effects, including bandgap renormalization and change in exciton binding energy, play only negligible roles. It is worthwhile to point out that previous studies have reported electrically tunable light absorption and emission of
monolayer TMDC materials [66-71], but this work is the first ever quantitatively demonstrating the gated tunability in refractive index as well as the dominating mechanism.

### 3.2 Analysis of gating refractive index

We start with examining the spectral reflection of TMDC monolayers. Figure 1a inset schematically illustrates the measurement configuration. The monolayers are grown on degenerately doped Si substrates with thermally grown silicon oxide (SiO$_2$/Si) using well established chemical vapor deposition (CVD) processes.[72, 73] The source and drain electrodes are fabricated on top of the monolayer using standard e-beam lithography and metallization procedures. We have confirmed that the electrodes form Ohmic contact with the monolayers. In the experiments, the Si substrate is used as the gate and the potentials at the source and drain electrodes are kept to be the same. Fig 3.1a shows the spectral reflection collected from monolayer WS$_2$ under different gating voltages.
Figure 3.1. Gated reflection and refractive index of monolayer WS2. (a) Reflection spectra of monolayer WS2 at different gating voltages. The inset is schematic illustration for the measurement configuration. The two arrows point out the two excited states of the A exciton, 2S and 3S. (b) Fitted real part $n$ and imaginary part $k$ of refractive index with different gating voltages. (c) The peak value of the real part (at around 1.92 eV) and the imaginary part (at around 1.95 eV) as a function of carrier densities.

The reflection of the A exciton shows substantial variation with the gating voltage, while the variation is much less at the B exciton and essentially negligible at the C exciton (Fig. 3.2).

Figure 3.2 Gated reflection of monolayer WS2 around C exciton.
The appearance of reflection change only at the excitonic peaks suggests that the variation is not caused by the plasma dispersion effect of free charge carriers as reported in previous studies[54-58], which would otherwise lead to changes over a broad spectral range. Similar gating effects in reflection can also be observed at monolayer MoS$_2$ and WSe$_2$ (Fig. 3.3).

![Figure 3.3](image_url)

**Figure 3.3** Spectral reflection collected from (a) monolayer MoS$_2$ and (b) monolayer WSe$_2$ under different gating voltages.

Of our interest is to find out how the refractive index of the monolayer may be tuned by the electrically gating. We can extract out the information of refractive index by fitting the measured reflection with a combination of multi-Lorentzian and multilayer reflection modeling. Basically, we fit the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ of the monolayer as a sum of contribution from multiple Lorentz oscillators[74, 75]:

$$\varepsilon(E) = \varepsilon_\infty + \sum_j \frac{f_j}{E_j^2 - E^2 - iE\gamma_j}$$  \hspace{1cm} (3.2.1)
where $\varepsilon_\infty$ is the high frequency dielectric constant, $E_j$ and $\gamma_j$ are the resonant energy and damping factor of the $j$th oscillator, respectively. $f_j$ is a phenomenal parameter involving contribution from the transition matrix element, density of states, and excitonic effects. Additionally, we fit the reflection of the monolayer on top of SiO$_2$/Si substrates using a model for the reflection of multilayer structures as[76]

$$R = |r|^2 = \left| \frac{\rho_1 + \rho_2 e^{-i2k_1d_1} + \rho_2\rho_3 e^{-i2k_2d_2} + \rho_3 e^{-i2(k_1d_1+k_2d_2)}}{1 + \rho_2\rho_1 e^{-i2k_1d_1} + \rho_2\rho_3 e^{-i2k_2d_2} + \rho_3 e^{-i2(k_1d_1+k_2d_2)}} \right|^2$$

(3.2.2)

where $\rho_1 = (n_1 - n_0)/(n_1 + n_0)$, $\rho_2 = (n_2 - n_1)/(n_1 + n_2)$, and $\rho_3 = (n_3 - n_2)/(n_2 + n_3)$. $n_0$, $n_1$, $n_2$, and $n_3$ are the refractive index of air, the monolayer, SiO$_2$, and Si, respectively. $k_1$ and $k_2$ are the wavenumber in the monolayer and SiO$_2$ as $k_1 = n_1\pi/\lambda$ and $k_2 = n_2\pi/\lambda$. $d_1$ and $d_2$ are the thickness of the monolayer and the SiO$_2$. The refractive index of the monolayer $n_2$ can be correlated to the fitted dielectric function $\varepsilon$ as $n_2^2 = \varepsilon$. The fitting mainly focuses on the spectral range shown in Fig.1a as the dielectric function outside this spectral range only negligibly varies with the gating voltage (see more details of the fitting in the Supporting Information). Three major oscillators are involved in this spectral range, including the neutral A exciton ($A_0$), the charged A trion (A or $A_+$), and the B exciton (B). The resonant energy $E_j$ and damping factor $\gamma_j$ of each of the oscillators can be found out from the measured spectral reflection. There are another two small oscillators corresponding to the excited states (2S and 3S) of the A exciton as indicated by the black arrows in Fig. 3.1a [77] but excluding them may not cause much difference in the fitting. As a result, the only parameters in Eqs. (3.2.1)-(3.2.2) that we need to fit are the $f_j$ of $A_0$, $A_+$, and B.
Figure 3.4. Fitted (dash lines) and measured (solid lines) spectra reflection of monolayer WS\textsubscript{2} under different gate voltages. In this fitting, the dielectric function is fitted using the multi Lorentzian model.

Fig. 3.1b shows the refractive index obtained from the fitting. We also plot the fitted reflection spectra along with the experimental result (Fig. 3.4), the consistence of which supports the validity of the fitting. The refractive index at the frequencies close to the A exciton shows substantial tunability, with the real part tuned from 4.80 to 3.97 and the imaginary part from 1.7 to 0.7 when the gating voltage $V_g$ is changed from 0 to 67 V. This is two orders of magnitude higher than what previously reported for tuning the refractive index by electrical gating [78]. Note that the maximal tunability of the real and imaginary parts appears at different frequencies, 1.95 eV for the imaginary part and around 1.92 eV for the real part. This is rooted in the conjugation nature of the real and imaginary parts of dielectric functions. To further illustrate the tunability, we plot the real part of the refractive index at 1.92 eV and the imaginary part at 1.95 eV as a function of the density of charge carriers in
The charge density is estimated using the capacitor model \( Q = C_{ox}(V_g - V_{th}) \), in which \( C_{ox} \) is the oxide capacitance, \( V_g \) is the gate voltage, and \( V_{th} \) is the threshold voltage for charge neutrality in the monolayer that we find to be around 6V from PL and I-V measurements (Fig. 3.5). Both the real and imaginary parts of the refractive index show a maximum at the point of charge neutrality, and decrease with the density of charge carriers increasing.

The observed tunability in refractive index can be mainly correlated to the absorption of the neutral A exciton (A\(_0\)). This is evidenced by the imaginary part of the fitted dielectric function \( \varepsilon_2 \) (Fig. 3.6), which shows substantial variability only at A\(_0\). Generally, the imaginary part of dielectric functions is linearly proportional to optical absorption and may uniquely determine the real part of the dielectric function via the Kronig-Kramers relationship [75].
Figure 3.6. Fitted real (upper) and imaginary (lower) parts of dielectric function under different gate voltages.

The peak absorption of $A_0$ is linearly proportional to $\varepsilon_2 = f_{A0}/(E_{A0} \gamma_{A0})$. As the resonant frequency $E_{A0}$ does not change much with the gating voltage (Fig. 3.7a), the tunability in the refractive index can be further ascribed to the gated variation of $f_{A0}$ and $\gamma_{A0}$. To better illustrate the variation, we plot the $\gamma$ and fitted $f$ of $A_0$ as a function of charge carrier densities in Fig. 3.7b-c. The result for the charged A exciton ($A_{+/–}$) is also plotted as reference.
Figure 3.7 Tunability of physical parameters in monolayer WS$_2$. (a) Optical bandgap $E$, (b) damping factor $\gamma$, and (c) $f$ that representing the oscillation strength of the neutral ($A_0$) and charged A ($A_{+/−}$) excitons.

3.3 Effects of gating induced charge carrier injection

We can find out the physical mechanism dominating the gated variation of $f$ and $\gamma$ by quantitatively examining the effects of free charge carriers. Generally, free charge carriers may affect the optical properties of low-dimensional semiconductor materials through three major physical mechanisms: Pauli blocking, Coulomb scattering, and dielectric screening. While these effects have previously been discussed for monolayer TMDC materials [66-71], there is no study on how each of the mechanisms may affect the refractive index. The Pauli blocking effect is expected to be negligible for the neutral A exciton in monolayer WS$_2$, because the injected electrons tend to fill in a lower-lying spin-orbit-split level of the conduction band that is not involved in the absorption of the neutral A exciton[66]. The Coulomb scattering, by which excitons scatter with free charge carriers, may broaden
excitonic absorption and also facilitate the formation of charged excitons. The screening of Coulomb interactions may lead to bandgap renormalization and decrease in the exciton binding energy \([77, 79, 80]\). We believe that the Coulomb scattering is the major mechanism for the observed increase in the damping factor \(\gamma\), because there is no change in the other factors like electron-phonon scattering or defect scattering that may induce homogeneous or inhomogeneous broadening to the absorption \([81]\). As a result, the focus of our analysis is to evaluate how the Coulomb scattering and the screening of Coulomb interactions may affect the \(f\).

![Figure 3.8](image-url) **Figure 3.8.** Bandgap renormalization and change in exciton binding energy in monolayer WS\(_2\). (a) Comparison of Raman spectra of monolayer WS\(_2\) at different temperatures (left) and different gating voltages (right). The intensity is normalized to that of the \(A_{1g}\) peak. (b) The measured (red dots) and fitted (blue line) Raman intensity ratio as a function of the temperature (red dots). The black curve is the calculated bandgap shift of the monolayer as a function of temperature, in which the bandgap at 300 K is used as the reference. The dashed lines indicate one Raman intensity ratio measured at the monolayer under electrically gating. (c) The estimated bandgap renormalization of monolayer WS\(_2\) as a function of the density of charge carriers.
The bandgap renormalization and the change in binding energy caused by the screening of Coulomb interactions can be evaluated from Raman measurements. The intensity ratio of the two characteristics Raman peaks of monolayer WS$_2$, $E_{2g}/2LA(M)$ and $A_{1g}$, decreases with the charge carrier density increasing (Fig. 3.8a). This may be correlated to the bandgap renormalization as the intensity of the $E_{2g}/2LA(M)$ peak is known to be related with the bandstructure due to the involvement of double resonance[82]. We can estimate the amplitude of the bandgap renormalization by comparing the Raman spectra measured at different gating voltages to those collected under different temperatures, the latter of which show a similar decrease in the Raman intensity ratio with the temperature increasing (Fig. 3.8a). Briefly, we identify the temperature with Raman intensity ratio comparable to what observed with the electrical gating, and then estimate the bandgap renormalization based on a well established temperature-bandgap correlation (Fig. 3.8b) [83]. The estimated bandgap renormalization is plotted as a function of the density of charge carriers in Fig. 3c, in which the bandgap at 0V is used as the reference point. With the knowledge of the bandgap renormalization $\Delta E_g$, we can derive the change in binding energy $\Delta E_{ex}$ from the change in the optical bandgap $\Delta E_{opt}$ as $\Delta E_{opt} = \Delta E_g - \Delta E_{ex}$. For the neutral A exciton, the change in the binding energy is approximately the same as the bandgap renormalization since the optical bandgap only shows mild variation ($< 7$ meV) with the electrical gating (Fig. 3.7a). With reasonably analysis, we may also find the change in binding energy for the charged A exciton to be less than 10 meV (Fig. 3.9).
Figure 3.9. Change in the binding energy of charged A exciton as a function of the gating voltage. The binding energy of the charged A exciton can be calculated as $E_{A0} - E_{A^{+/−}} - E_F$, where $E_{A0}$ and $E_{A^{+/−}}$ are the optical bandgap of the neutral and charged A excitons, respectively. $E_F$ is the fermi energy shift with respect to the minimum of conduction band caused by the injected charge carriers. It can be calculated from the charge density $n$ and the density of state in 2D system as $E_F = \hbar^2 \pi n / (2m^*e^2)$. The change in the binding energy is the different between the binding energy under electrical gating and that at the charge neutral point.

3.4 Fractional dimensional space model analysis

We can quantitatively evaluate the contribution of the change in binding energy $\Delta E_{ex}$ and the bandgap renormalization $\Delta E_g$ to the tunability in dielectric function by fitting the dielectric function with a model of Wannier excitons in fractional dimension space. The fractional dimensional space model has been established to describe the optical properties of quantum wells. [84-87] It treats highly confined anisotropic excitons in low-dimensional structures to be isotropic in a fractional-dimensional space, and defines an effective dimensionality $d$ based on the binding energy in bulk materials $R$ and the low-dimensional structure $E_{ex}$ as $d = 1 + 2(R / E_{ex})^{0.5}$. One major advantage of the fractional dimension space model lies in its capabilities to separately evaluate the contribution of each individual variable to dielectric
According to the fractional dimension space model, the complex dielectric function $\varepsilon_j$ at an arbitrary energy $E$ contributed by one excitonic transition can be written as a product of a parameter representing the transition probability $S_j$ and a parameter involving excitonic effects, density of states, and electronic bandgap $G_j$, $\varepsilon_j = S_j G_j$. [84-87]

$$S_j = p_{vc}^2 \frac{2e^2}{\varepsilon_0 m_0^2} \left( \frac{\mu}{2\pi} \right)^{d/2} \Gamma(2 - \frac{d}{2})$$

$$G_j = \frac{R^2}{(E + i\gamma_j)^2} [g_d(\xi(E + i\gamma_j)) + g_d(\xi(-E - i\gamma_j)) - 2g_d(\xi(0))]$$

$$g_d(\xi) = \frac{2\pi \Gamma(\frac{d-1}{2} + \xi)}{\Gamma(\frac{d-1}{2}) \Gamma(1 - \frac{d-1}{2} + \xi) \xi^{d-2}} [\cot \pi(\frac{d-1}{2} - \xi) - \cot \pi(d - 1)]$$

(3.4.1)

where $p_{vc}$ is the matrix element for the transition from valance band to conduction band, $\mu$ is the reduced effective mass of electrons, $e$ and $m_0$ are the charge and mass of free electrons, $\varepsilon_0$ and $\hbar$ are vacuum permittivity and Planck’s constant, $\Gamma()$ is the Euler function, $\xi()$ is a function related with the electronic bandgap $E_g$ and $R$ as $\xi(z) = [R/(E_g - z)]^2$. We use the Eqs. (3.4.1) to fit the dielectric function as well as the measured spectral reflection. The exciton binding energy in monolayer and bulk WS2 is 0.7eV [15, 16] and 0.055 eV [88], respectively. The other parameters, including the effective dimensionality $d$, electronic bandgap $E_g$, damping factor $\gamma$ can be obtained from either the binding energy, the experimental measurement, or the above-mentioned discussion. In the fitting, we first calculate $G_j$ using these parameters and then fit the value of $S_j$ to match the dielectric function and the measured reflection spectra (Fig. 3.10).
Figure 3.10. Fitted (dash lines) and measured (solid lines) spectra reflection of monolayer WS\textsubscript{2} under different gate voltages. The dielectric function is fitted using the Fractional dimensional space model.

The fitting result indicates that the change in binding energy $\Delta E_{\text{ex}}$ and the bandgap renormalization $\Delta E_g$ play negligible roles in the tunability of the dielectric function. It also indicates that the gated variation in $f_{A0}$ mainly results from the interchange of intrinsic transition probabilities between the neutral and charged excitons. Fig. 3.11(a-b) shows the fitted $S_j$ and calculated $G_j$ for the neutral A exciton at different carrier densities.
**Figure 3.11.** Dominating mechanism for the tunable refractive index. (a) Fitting results for $S$ and $f$ of the neutral and charged A excitons as function of charge carrier densities. (b) Calculated $G$ for the neutral A exciton with different gating voltages. (c) Calculated $G$ of the neutral A exciton as a function of (upper) change in exciton binding energy, (middle) bandgap renormalization, (c) change in the damping factor $\gamma$. The spectra in the upper and middle panels are artificially shifted to align the peak position for the convenience of comparison.

The fitted $S_j$ for the charged A exciton is also plotted in Fig. 3.11a. $S_j$ is essentially a product of the intrinsic transition probability $p_{vc}$ by a constant, as the effective dimensionality $d$, which is related with the change in binding energy $\Delta E_{ex}$, varies less than 2% in our experiments. We can get useful physical insight by comparing $S_j$ to $f_j$ as shown in Fig. 3.11a. The results are all normalized to the sum of the value for both neutral and changed excitons ($S_{A0} + S_{A+/−}$ and $f_{A0} + f_{A+/−}$) at 0V for the convenience of comparison. The $S_j$ and $f_j$ show similar dependence on the charge carrier density. This indicates that the enhancement by
excitonic effects to the oscillation strength, which is involved in $f_j$ but not in $S_j$, does not change much with the gating voltage. In another word, the variation in the $f_j$ results from change in the transition matrix element $p_{vc}$, instead of excitonic effects. We can get more insight by examining the $S_j$ for the neutral and charged excitons together. The sum of the $S_j$ for the neutral and charged excitons together remains to be reasonably constant regardless the gating voltage. This suggests that the intrinsic transition probability (transition matrix element) $p_{vc}$ for the neutral and charged excitons interchange with electrical gating while their sum maintain to be reasonably constant. Additionally, we examine $G_j$ as a function of one variable with the other two kept to be constant, including the change in binding energy $\Delta E_{ex}$ that is included in the effective dimensionality $d$, the bandgap renormalization $\Delta E_g$ that is included in the electronic bandgap $E_g$, and the damping factor $\gamma$ (Fig. 3.11c). This allows us to check the effect of each individual variable on the dielectric function. The calculation results indicates very mild effect (less than 10%) of the change in binding energy $\Delta E_{ex}$ and the bandgap renormalization $\Delta E_g$ on the $G_j$. The dominant cause for the variation in the $G_j$ is the change in the damping factor $\gamma$.

3.5 Conclusion

We can conclude that the tunability in the refractive index of TMDC monolayers is mainly due to the spectral broadening and inter-transfer of intrinsic transition probability (transition matrix element) between the neutral and charged excitons, both of which are related with the Coulomb scattering by free charge carriers. In contrast, the bandgap renormalization and change in exciton binding energy caused by the screening of Coulomb interaction only play negligible roles. The result provides new insight into the fundamental optical properties of
two-dimensional materials. For instance, it indicates that the substrate and dielectric environment may not affect the dielectric function of 2D TMDC materials much [65], unless strong doping to the materials is involved [89]. More importantly, this substantial tunability in refractive index by electrical gating may open up a new age of field-effect photonics in which the functionality of optical devices can be electrically controlled in a way similar to that of state-of-art CMOS circuits.
CHAPT 4: Fundamental Limits of Exciton-Exciton Annihilation for Light Emission in Transition Metal Dichalcogenide Monolayer

We quantitatively illustrate the fundamental limit that exciton-exciton annihilation (EEA) may impose to the light emission of monolayer transition metal dichalcogenide (TMDC) materials. The EEA in TMDC monolayers shows dependence on the interaction with substrates as its rate increases from 0.1 cm$^2$/s (0.05 cm$^2$/s) to 0.3 cm$^2$/s (0.1 cm$^2$/s) with the substrates removed for WS$_2$ (MoS$_2$) monolayers. It turns to be the major pathway of exciton decay and dominates the luminescence efficiency when the exciton density is beyond $10^{10}$ cm$^{-2}$ in suspended monolayers or $10^{11}$ cm$^{-2}$ in supported monolayers. This sets an upper limit on the density of injected charges in light emission devices for the realization of optimal luminescence efficiency. The strong EEA rate also dictates the pumping threshold for population inversion in the monolayers to be 12-18 MW/cm$^2$ (optically) or $2.5-4 \times 10^5$ A/cm$^2$ (electrically).

4.1 Introduction

Two-dimensional (2D) transition metal dichalcogenide (TMDC) materials such as monolayer MoS$_2$ and WS$_2$ promise to enable the development of atomic-scale light emission devices owing to their semiconducting nature, perfect surface passivation, and strong exciton binding energy [29]. A key issue for the device development is to understand the exciton dynamics of these materials, which has been known bearing substantial difference from what observed at conventional materials. In particular, the extraordinary exciton binding energy in the TMDC monolayers [17, 90-92] is expected to enable strong many-body interactions like exciton-exciton annihilation (EEA). Recent studies have demonstrated that the EEA rate in
monolayer TMDC materials is indeed two orders of magnitude higher than that in conventional semiconductor materials [93-96]. However, much fundamental of the EEA has remained to be elusive. For instance, substantial discrepancy can be found in the previous studies as some reported negligible EEA in the monolayers[97-99] shown to have strong EEA by others[94, 95]. It is also not clear how the EEA could depend on the nature of the materials and the environment at the proximity like substrates. Most importantly, although it is generally known that EEA may affect luminescence efficiency, there is no quantitatively understanding about how the strong EEA could affect the light emission efficiency of the monolayers in unusual ways. This understanding would provide useful guidance for the rational design of high-performance light-emission devices.

4.2 Measurement of power dependent light emission efficiency of suspended and supported monolayer TMDC

Fig. 4.2.1a-b shows the PL efficiencies (the number of emitted photons vs. the number of adsorbed photons) of suspended monolayer MoS$_2$ and WS$_2$ as a function of incident laser power. The samples were prepared by manually transferring chemical vapor deposition-grown monolayers from the growth substrate (sapphire) onto SiO$_2$/Si substrates pre-patterned with holes Fig. 4.2.2 [100].
Figure 4.1. PL efficiencies of (a) suspended monolayer WS$_2$, (b) suspended monolayer MoS$_2$, (c) as-grown monolayer WS$_2$ on sapphire substrates, and (d) as-grown monolayer MoS$_2$ on sapphire substrates as a function of the incident power density. The dashed lines are simulation results using Eq. (4.4.3) and the parameters given in Table 1. The insets in (a) and (b) are to better illustrate the results in the corresponding dashed box. All the given error bars are 10%. The error bars in the (a) and (b) are ignored for visual convenience.

Figure 4.2. Optical image of typical as-grown monolayers on sapphire substrates and transferred monolayers on SiO$_2$/Si substrates pre-patterned with holes. The black areas are the pre-patterned holes on the substrate.

The efficiency is evaluated from PL measurements at room temperature with Rhodamine 6G used as a reference. While the efficiencies vary among these materials, all exhibit an
exponential decrease with the incident power increasing, even at an incident power as low as 10 W/cm$^2$. In stark contrast, the PL efficiencies of the as-grown monolayers show much milder dependence on the incident power (Fig. 4.2c-d). We can exclude out any substantial heating effects and the formation of bi-excitons in the measurement as the lineshape and position of the PL show negligible change through the measurement (Fig. 4.3). It has been known that the PL would redshift or broaden at elevated temperatures and show new peaks at lower energy with the formation of bi-excitons [101-103].

![Figure 4.3](image)

**Figure 4.3.** Dependence of the PL spectra of suspended MoS$_2$ and WS$_2$ on incident power. (a) PL spectra of suspended MoS$_2$ at different incident powers. Inset: Zoom-in curves of 4 representative powers, the black dash lines denotes PL peak position at the lowest and highest incident powers used in the experiments. The temperature change in the sample can be estimated by this peak shift ($\sim 8$ meV) using the well-established temperature dependent bang-gap equation $E_g(T) = E_g(0) - \alpha T^2 / (T + \beta)$ and $\alpha = 5.9 \times 10^{-4} eV / K$, $\beta = 430K$ from Ref.S3, the temperature change is calculated to be around 20K with the incident power 50 $\mu$W/cm$^2$. (b) PL spectra of suspended WS$_2$ at different incident powers. Similar to suspended MoS$_2$, the peak shift is small and there is essentially no change in the PL lineshape.
With the exclusion of heating effects and biexcitons, the observed power-dependent PL efficiency may be correlated to another non-linear process: exciton-exciton annihilation (EEA).

4.3 Measurement of power dependent exciton dynamics of monolayer TMDC

To better understand the EEA, we examined the exciton dynamics in the suspended monolayers using pump-probe techniques. What we measured is the differential reflection $\Delta R/R$ of a delayed probe beam from the monolayers photoexcited by a pump beam (590 nm). The wavelength of the probe beam is chosen to match the $A$ exciton of the monolayer, and the pumping fluence is set to be small enough to ensure the absorption far below saturation. As a result, the differential reflection ($\Delta R/R$) can be linearly correlated to the density of photo-generated charge carriers at the band edges. Fig. 4.4 and Fig. 4.5 shows the transient differential reflection $\Delta R/R$ collected from suspended WS$_2$ monolayers suspended MoS$_2$ monolayers. We confirmed no substantial heating effect in the experiments by ensuring a reasonable linear dependence of the $\Delta R/R$ at the 0s delay ($\Delta R/R_0$) on the pumping fluence because ($\Delta R/R_0$) is sensitive to the temperature (Fig. 4.6). The decay rate can be found increasing with the pumping fluence (Fig. 4.4a), consistent with what expected from EEA. The increase of the decay rate also indicates negligible formation of bi-excitons, which would otherwise show the decay rate slowing with the pump fluence increasing [104].
Figure 4.4. (a) Normalized differential reflection of suspended WS\textsubscript{2} with different pumping fluences, 1.5 \(\mu\text{J/cm}^2\) (red), 2.5 \(\mu\text{J/cm}^2\) (blue), and 5.0 \(\mu\text{J/cm}^2\) (black). Inset: the results for the early stage of the decay. (b) The result of \((\Delta R/R)_0/(\Delta R/R)_t\) -1 derived from the data in (a). The dashed line serves to illustrate the slope of the result. (c) Fitting for the measured differential reflection of suspended WS\textsubscript{2} with different pumping fluences as labeled. The fitted results are plotted in dashed lines and the experimental results are dots.

Figure 4.5. (a) Normalized differential reflection of suspended MoS\textsubscript{2} as a function of the time delay and with different pumping fluences, 1.5 \(\mu\text{J/cm}^2\) (red), 2.5 \(\mu\text{J/cm}^2\) (black), and 5.0 \(\mu\text{J/cm}^2\) (blue). Inset: the results for the early stage of the decay. (b) The result of \((\Delta R/R)_0/(\Delta R/R)_t\) -1 derived from the data in (a) as a function of the delay time. The result for the pumping fluence of 5.0 \(\mu\text{J/cm}^2\) is not shown for the visual convenience. (c) Fitting for the measured differential reflection of suspended MoS\textsubscript{2} with different pumping fluences, The
fitted results are plotted in dashed lines and the experimental results are dots, 1.5 µJ/cm² (red), 2.5 µJ/cm² (black), and 5.0 µJ/cm² (blue).

Figure 4.6. Transient reflection ΔR/R measured at the supported monolayer MoS2 on sapphire substrates at different temperatures, 75K, 150K, 220K, and 295K. The ΔR/R at the 0s delay exhibits a strong dependence on the temperature.

We can evaluate the rate constant of the EEA based on the pump-probe measurement. Should the exciton decay be dominated by EEA, the rate equation of exciton density would be written as a function of the EEA rate \( k_{ee} \), \( dN/dt = -k_{ee}N^2 \). And the exciton density \( N(t) \) would be correlated to the total photo-generated excitons \( N_0 \) as

\[
\frac{N_0}{N(t)} - 1 = k_{ee}N_0t
\]  

(4.3.1)

As \( \Delta R/R \) can be linearly correlated to the density of photo-generated charge carriers, we may have \( N_0/N(t) = (\Delta R/R)_0/(\Delta R/R)_t \). We can derive \( (\Delta R/R)_0/(\Delta R/R)_t \) -1 from the result given in Fig. 4.4a and Fig. 4.5a, and plot it as a function of the delay time in Fig. 4.4b and Fig. 4.5b. The result shows that \( (\Delta R/R)_0/(\Delta R/R)_t \) -1 linearly depends on the delay time at the early stage.
of the decay (up to 50-100 ps) and its slope linearly increases with the pumping fluence (Fig. 4.4b and Fig. 4.5b). This is consistent with what expected from Eq. (4.3.1), indicating that the early-stage exciton decay in the suspended monolayer is dominated by EEA. We can also estimate the total photo-generated excitons \( N_0 \) from the incident fluence and the absorption efficiency of the monolayers. The absorption of suspended WS\(_2\) and MoS\(_2\) for the pump beam is estimated to be 0.058 and 0.022, respectively, using the refractive index we measured (See [19] and Fig. 4.10). The rate constant \( k_{ee} \) can thus be derived from the slope in Fig. 4.4b anf Fig. 4.5b as 0.3 \( \text{cm}^2/\text{s} \) and 0.1 \( \text{cm}^2/\text{s} \) for suspended WS\(_2\) and MoS\(_2\) monolayers, respectively.

**Figure 4.7.** (a) Normalized differential reflection of as-grown WS\(_2\) as a function of the time delay and with different pumping fluences, 10 \( \mu \text{J/cm}^2 \) (red), 25 \( \mu \text{J/cm}^2 \) (black), and 50 \( \mu \text{J/cm}^2 \) (blue). Inset: the results for the early stage of the decay. (b) The result of \( (\Delta R/R)_0/\Delta R/R \) derived from the data in (a) as a function of the delay time. The result for the pumping fluence of 50 \( \mu \text{J/cm}^2 \) is not shown for the visual convenience. (c) Fitting for the measured differential reflection of as grown WS\(_2\) with different pumping fluences, The fitted results are plotted in dashed lines and the experimental results are dots, 10 \( \mu \text{J/cm}^2 \) (red), 25 \( \mu \text{J/cm}^2 \) (black), and 50 \( \mu \text{J/cm}^2 \) (blue).
Figure 4.8. (a) Normalized differential reflection of as-grown MoS<sub>2</sub> as a function of the time delay and with different pumping fluences, 25 µJ/cm<sup>2</sup> (red), 50 µJ/cm<sup>2</sup> (black), and 100 µJ/cm<sup>2</sup> (blue). Inset: the results for the early stage of the decay. (b) The result of \((\Delta R/R)_0/(\Delta R/R)_1\) -1 derived from the data in (a) as a function of the delay time. The result for the pumping fluence of 100 µJ/cm<sup>2</sup> is not shown for the visual convenience. (c) The non-normalized differential reflection of as-grown MoS<sub>2</sub> at pumping fluence 25 µJ/cm<sup>2</sup> (red), 50 µJ/cm<sup>2</sup> (black), and 100 µJ/cm<sup>2</sup> (blue).

Figure 4.9. \((\Delta R/R)_0/(\Delta R/R)_1\) -1 of (a) as-grown MoS<sub>2</sub> and (b) as-grown WS<sub>2</sub>. The results are derived from the differential reflection measurement at these materials with different pumping fluences as labeled.
To understand the different power dependence of PL efficiency in the supported monolayers, we performed similar pump-probe measurements and data analysis for the as-grown MoS$_2$ and WS$_2$ monolayers onto sapphire substrates (Fig. 4.7-9). The EEA rate is found to be 0.1 cm$^2$/s and 0.05 cm$^2$/s for the supported WS$_2$ and MoS$_2$, respectively. This smaller EEA rate indicates the effect of substrates, which may be understood from an intuitive perspective. Generally, the rate of EEA is related with the diffusion coefficient of excitons $D$ and the annihilation radius $R$ that represents the separation of two excitons when the annihilation may occur, $k_{ee} = 4\pi DR$ [105]. The presence of substrates may lower charge mobility and hence the diffusion coefficient [106]. The substrate may also lower the exciton binding energy[80, 107], which could subsequently lead to a smaller $R$. Additionally, the substrate may facilitate defect-assisted recombination that can compete with the EEA as a pathway for excitons to decay [98, 108]. While the presence of defect-assisted recombination may not change the EEA rate, it could make the experimental observation of the EEA more difficult, particularly when the defect-assisted decay rate is comparable to or even faster than the EEA rate. For instance, the EEA in the as-grown MoS$_2$ can be observed only in the first several ps (< 2 ps) and with relatively high pumping fluence (> 25 µJ/cm$^2$) (Fig. 4.8). We found in experiments that generally it was generally more difficult to observe the EEA in the monolayers showing lower PL intensities. Given the significant effect of substrates on the EEA, we believe that the discrepancies in the previous studies, i.e., the demonstration of different EEA rates in the same materials [94, 95, 97-99], is likely due to difference in the effect of substrates.
We can better understand the effect of the EEA on luminescence efficiency (Fig. 4.1) by correlating the power-dependent efficiency to the nonlinear and linear decay processes involved. The rate equation of exciton density for the time-averaged PL can be written as

$$\frac{dN}{dt} = -\left(\frac{1}{\tau_r} + \frac{1}{\tau_{nr}}\right)N - k_{ee}N^2 + \alpha I_0$$

(4.3.2)

where $\tau_r$ and $\tau_{nr}$ represent the exciton lifetimes associated with radiative and linear non-radiative recombinations, $\alpha$ and $I_0$ are the absorption efficiency for the incident wavelength and the incident power density. From eq. (2) we can derive the efficiency of the time-averaged PL as

$$QY = \frac{N/\tau_r}{\alpha I_0} = \frac{\sqrt{(1/\tau_r + 1/\tau_{nr})^2 + 4k_{ee}\alpha I_0} - (1/\tau_r + 1/\tau_{nr})}{2k_{ee}\alpha I_0\tau_r}$$

(4.3.3)

The absorption efficiency $\alpha$ of suspended monolayer MoS$_2$ and WS$_2$ can be calculated using the refractive index we measured (See [19] and Fig. 4.10), which is 0.065 and 0.055 for the incidence of 532 nm, respectively.
Figure 4.10. Measured refractive index of monolayer WS\(_2\). (a) measured real and imaginary part of the refractive index of monolayer WS\(_2\). (b) measured and fitted transmission of as-grown monolayer WS2 on sapphire substrates. The fitting results uses the refractive index given in (a).

The EEA rate \(k_{ee}\) is known from the differential reflection measurement. Then we can evaluate \(\tau_r\) and \(\tau_{nr}\) by numerically fitting the measured power-dependent efficiency to Eq. (4.3.3). The fitting results are plotted (dashed lines) along with the experimental results in Fig. 4.1 and the fitted value of \(\tau_r\) and \(\tau_{nr}\) are given in Table 1.

![Figure 4.10](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>(k_{ee}) (cm(^2)/s)</th>
<th>(\tau_r) (ns)</th>
<th>(\tau_{nr}) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sus WS(_2)</td>
<td>0.3</td>
<td>1</td>
<td>0.76</td>
</tr>
<tr>
<td>AG WS(_2)</td>
<td>0.1</td>
<td>4.5</td>
<td>0.13</td>
</tr>
<tr>
<td>Sus Mo(_S_2)</td>
<td>0.1</td>
<td>28</td>
<td>1</td>
</tr>
<tr>
<td>AG Mo(_S_2)</td>
<td>0.05</td>
<td>80</td>
<td>0.05</td>
</tr>
</tbody>
</table>

4.4 Derivation of population inversion in monolayer TMDC

This result may provide useful guidance for the rational design of light emission devices with optimal efficiency. It can guide the proper charge injection in light emission devices for the realization of optimal quantum yield. According to Eq. (4.3.2), the EEA may turn to be the
major pathway of exciton decay \((k_{ee}N^2 > (1/\tau_r + 1/\tau_{nr})N)\) when the exciton density \(N > (1/\tau_r + 1/\tau_{nr})/k_{ee}\), which is in the scale of \(10^{10}\) cm\(^{-2}\) and \(10^{11}\) cm\(^{-2}\) for suspended and supported monolayers, respectively. The charge injection must be controlled to maintain the steady-state charge density well below those values. We can estimate the steady-state charge density as a function of the injected current density \(J\) using an equation modified from Eq. (4.3.2), and get Eq. (4.4.1).

\[
N = \left[\sqrt{(1/\tau_r + 1/\tau_{nr})^2 + 4k_{ee}J} - (1/\tau_r + 1/\tau_{nr})\right]/2k_{ee}
\] 

Eq. (4.4.1)

The calculation indicates that, in order to maintain the steady-state charge density well below (<10\%) of the threshold values, the injected current density should be no more than 0.2-0.4 A/cm\(^2\) and 15-30 A/cm\(^2\) for suspended and supported monolayers, respectively (Fig. 4.11). Additionally, the result may help predict the lasing threshold and optical gain coefficient. We use a simple three-level system to represent the pumping process in the monolayer (Fig. 4.11b inset), in which the charges at the ground state 1 (valence band edge) are first pumped to the upper pump level 3 (a higher level in the conduction band) and then quickly decay to the level 2 (conduction band edge). The rate equation for the charge density at the level 2 can be written as

\[
\frac{dN_2}{dt} = -\sigma_{12} \frac{I}{h\nu_{12}} (N_2 - N_1) - \left(\frac{1}{\tau_r} + \frac{1}{\tau_{nr}}\right)N_2 - k_{ee}N_2^2 + \sigma_{13} \frac{I_p}{h\nu_{13}} N_1
\]

Eq. (4.4.2)

where \(\sigma_{12}\) is the stimulated emission (absorption) cross section for the light in frequency \(\nu_{12}\) that matches the energy difference between the level 1 and level 2, \(I\) is the photon flux at the frequency of \(\nu_{12}\), \(h\) is the Planck’s constant, \(\sigma_{13}\) is the absorption cross section for the pumping light in frequency \(\nu_{13}\), and \(I_p\) is the pumping intensity. By using the steady state
(dN₂/dt = 0) and the conservation of charges (N₂ + N₁ = N_t, N_t is the total charge density), we can find out the population inversion (N₂ - N₁) as

\[
\Delta N = N_2 - N_1 = \frac{\sqrt{\left(1/\tau_r + 1/\tau_{nr} + W_p\right)^2 + 4k_{ee} W_p N_t} - \left(1/\tau_r + 1/\tau_{nr} + W_p\right)} - k_{ee} N_t}
\]

and the optical gain coefficient as \( \gamma = \sigma_{12} \Delta N \), where \( W_p = \sigma_{13} I_p / h \nu_{13} \) representing the pumping rate. In the process of deriving Eq. (4.4.3) we assume a small-signal inversion \( (I \ll I_p) \) and ignore the term of \( \sigma_{12} I / h \nu_{13} \). Based on the value given in Table 1, \( k_{ee} N_t / 2 \) is always one or two orders of magnitude larger than \( 1/\tau_r + 1/\tau_{nr} \) for all the supported and suspended monolayers. As a result, essentially the threshold pumping rate \( W_p = k_{ee} N_t / 2 \) as \( k_{ee} N_t / 2 \gg 1/\tau_r + 1/\tau_{nr} \).

And the population inversion can be simplified as

\[
\Delta N = \left(\sqrt{W_p^2 + 4k_{ee} W_p N_t} - W_p\right) / k_{ee} - N_t.
\]

The total charge density \( N_t \) in monolayer WS₂ and MoS₂ can be estimated to be \( 4.17 \times 10^{12} \text{ cm}^{-2} \) and \( 6.27 \times 10^{12} \text{ cm}^{-2} \) by assuming parabolic band edges at \( K \) point and using the average effective mass reported in the literature (\( 0.4m_0 \) and \( 0.6m_0 \) for WS₂ and MoS₂)[20, 109-111]. The stimulated emission (absorption) cross-section \( \sigma_{13} (\sigma_{12}) \) can be derived from the total charge density and the absorption efficiency \( \alpha_{13} (\alpha_{12}) \) as \( \sigma_{13} = \alpha_{13} / N_t (\sigma_{12} = \alpha_{12} / N_t) \). Without losing generality, we use the pumping wavelength of 532 nm as an example to implement numerical evaluation. Fig. 4.11b-c shows the calculated population inversion and optical gain coefficient as a function of the incident power at optically pumping (532 nm) and the injected current density at electrically pumping. The result indicates that the threshold is around 12-18 MW/cm² at optically pumping or 2.5-4 MA/cm² at electrically pumping. This calculation does not take into account any optical enhancement effects, heating effect during the pumping, and possible re-normalization of the bandgap [80, 112]. It nevertheless provides
This predicted threshold pumping power is reasonably consistent with one recent study, in which the threshold pumping power for lasing in supported WS\textsubscript{2} monolayer is estimated at 5-8 MW/cm\textsuperscript{2} [113].

**Figure 4.11.** (a) Steady-state charge density as a function of the injected current density in suspended monolayer MoS\textsubscript{2} (red), supported MoS\textsubscript{2} (black), suspended WS\textsubscript{2} (blue), and supported WS\textsubscript{2} (brown). The dash lines indicate the proper charge density and corresponding injection current density in order to have negligible effects from the EEA. (b) Calculated population inversion and (c) optical gain coefficients as a function of pumping power (optical) and injection current density (electrical) for different monolayers, including suspended monolayer MoS\textsubscript{2} (red), supported MoS\textsubscript{2} (black), suspended WS\textsubscript{2} (blue), and supported WS\textsubscript{2} (brown). Inset, a schematic illustration of the three-level model used for the calculation. The absorption efficiency is approximately set to be 5\% for the conversion of the pumping power to the injection current density.

**4.5 Conclusion**

In conclusion, we have quantitatively evaluated the EEA and its effect on light emission for suspended and supported monolayer TMDC materials. The EEA is subject to strong
influence of the substrate. It may turn to be the major pathway of exciton decay and dominates the luminescence efficiency when the exciton density is in scale of $10^{10}$ cm$^{-2}$ in suspended monolayers or $10^{11}$ cm$^{-2}$ in suspended monolayers. This sets an upper limit for the density of injected charges in light emission devices in order to achieve optimal luminescence efficiency. The strong EEA also dictates the pumping threshold for population inversion in the monolayers to be 12-18 MW/cm$^2$ at optically pumping or 2.5-4 MA/cm$^2$ at electrically pumping. The result may provide useful guidance for the rational design of atomic-scale light emission devices, including LEDs and lasers.
We demonstrate that the luminescence efficiency of monolayer MoS$_2$, WS$_2$, and WSe$_2$ is significantly limited by the substrate and can be improved by orders of magnitude through substrate engineering. The substrate affects the efficiency mainly through doping the monolayers and facilitating defect-assisted non-radiative exciton recombinations, while the other substrate effects including straining and dielectric screening play minor roles. The doping may come from the substrate and substrate-borne water moisture, the latter of which is much stronger than the former for MoS$_2$ and WS$_2$ but negligible for WSe$_2$. Using proper substrates such as mica or h-BN can substantially mitigate the doping effect. The defect-assisted recombination depends on the interaction between the defect in the monolayer and the substrate. Suspended monolayers, in which the substrate effects are eliminated, may have efficiency up to 40% at room temperatures. The result provides useful guidance for the rational design of atomic-scale light emission devices.

5.1 Introduction

Two-dimensional (2D) transition metal dichalcogenide (TMDC) materials such as monolayer MoS$_2$, WS$_2$, and WSe$_2$ promise to enable the development of atomic-scale light emission devices, but their luminescence efficiencies have been shown to be surprisingly low despite the materials’ perfect surface passivation and strong exciton binding energy[27, 29]. Recent studies indicate that the optical properties of 2D TMDC materials are susceptible to the influence of substrates[1, 114-123]. It has been reported that substrates may affect the luminescence efficiency of the monolayers by inducing strain, doping, or dielectric
screening[114, 117-119, 124]. However, despite the recent progress, many important questions about the substrate effect have remained to be answered. For instance, while it is known that substrates could affect the luminescence efficiency through multiple ways, there is no quantitative understanding for the effect of each mechanism and no knowledge on which mechanism could be dominant. More importantly, it is not clear how the effect of substrates might depend on the nature of the monolayers and the surface properties of the substrate. Answers to these questions would provide useful guidance for the realization of optimal luminescence efficiency through engineering the substrate effects.

5.2 Observation of huge light emission efficiency difference between suspended TMDC and supported TMDC

Here we quantitatively evaluate the effect of substrates on the luminescence efficiency of monolayer MoS$_2$, WS$_2$, and WSe$_2$, and demonstrate strategies of substrate engineering to improve the efficiency by orders of magnitude. We find that the main effects of the substrate lie in doping the monolayers and facilitating defect-assisted non-radiative exciton recombinations. The doping may be from substrate-borne water moisture and the substrate, the former of which is much stronger than the latter for WS$_2$ and MoS$_2$ but negligible for WSe$_2$. Using proper substrates can substantially mitigate the doping effect on the PL, such as mica for WS$_2$ and MoS$_2$ and h-BN or polystyrene for WSe$_2$. The defect-assisted recombination depends on the interaction of the defects in the monolayer such as sulfur vacancies with the substrate, and may be substantially suppressed by either removing the substrate or lowering the number of defects. In this work we largely ignore the optical resonance effects associated with the substrate’s geometrical features[125].
Figure 5.1. Improved luminescence efficiency of suspended monolayers. (a) Optical image of a typical suspended monolayer. Inset, an as-grown monolayer (scale bar: 10 µm). (b) Photoluminescence (PL) mapping of the suspended monolayer. The color bar of PL intensity is in logarithm scale. (c) PL spectra of as-grown monolayer MoS$_2$ on sapphire substrates, suspended monolayer MoS$_2$, and the monolayer MoS$_2$ transferred onto SiO$_2$/Si substrates with 300 nm thick thermally grown oxide. The spectra of the as-grown and the one on SiO$_2$/Si substrates are multiplied by a constant of 50 for visual convenience. (d) PL spectra of as grown monolayer WS$_2$, suspended monolayer WS$_2$, and the monolayer WS$_2$ transferred onto SiO$_2$/Si substrates. The spectra of the as-grown and the one on SiO$_2$/Si substrates are multiplied by 25 and 50, respectively.
Figure 5.2. Improved luminescence efficiency of suspended monolayer WSe\textsubscript{2}. PL spectra of as-grown monolayer WSe\textsubscript{2} on SiO\textsubscript{2}/Si substrate, suspended monolayer WSe\textsubscript{2}, and the monolayer WSe\textsubscript{2} transferred onto another SiO\textsubscript{2}/Si substrate. The spectra of the as-grown and transferred monolayers are multiplied by 15 for visual convenience.

We compare the PL of suspended MoS\textsubscript{2}, WS\textsubscript{2}, and WSe\textsubscript{2} monolayers to those of as-grown counterparts. The monolayers were synthesized on sapphire substrates using chemical vapor deposition (CVD) processes as described previously\textsuperscript{126}, and the suspended monolayers were prepared by manually transferring the synthesized monolayers onto SiO\textsubscript{2}/Si substrates pre-patterned with holes (Fig. 5.1a-b), which followed a surface-energy-assisted transfer technique that we previously developed (see Method)\textsuperscript{127}. Significantly, the suspended monolayers show PL intensities two orders of magnitude (~30-60 times) stronger than the as-grown counterparts under the same incident power (Fig. 5.1c-d and Fig. 5.2). The incident power used was very small (usually < 20 W/cm\textsuperscript{2}) to minimize potential heating effect and many body interactions\textsuperscript{128}. We evaluate the PL efficiency (the number of photons emitted vs. the number of photons absorbed) of the monolayers by using Rodamine
6G dye molecules as a reference. The typical PL efficiencies are found to be 0.13% and 4.1% for the as-grown and suspended MoS\(_2\), 2.3% and 40% for the as-grown and suspended WS\(_2\) monolayers, and 0.6% and 22% for the supported and suspended WSe\(_2\) monolayers, respectively.

**Figure 5.3.** Raman and PL mapping of as-grown MoS\(_2\) on sapphire substrates. (a) Mapping for the frequency of the E\(_{2g}^1\) peak (unit: cm\(^{-1}\)). (b) Mapping for the frequency of the A\(_{1g}\) peak (unit: cm\(^{-1}\)). (c) Mapping for the position of the PL peak (unit: nm). (d) Mapping for the PL intensity. We can find clear correlation between the PL intensity, the PL wavelength, and the frequency of the A\(_{1g}\) peak. Generally, weaker PL intensities can be correlated to redshifted A\(_{1g}\) peaks and longer PL wavelengths. This suggests that the variation in PL intensity is due to different local doping as more n-doping may give rise to redshifts in the A\(_{1g}\) peak, lower PL intensity, and longer PL wavelengths.
Figure 5.4. Raman and PL mapping for the monolayer MoS2 transferred on sapphire substrates. Mapping for (a) the frequency of the E2g1 peak, unit: cm$^{-1}$, (b) the frequency of the A1g peak, unit: cm$^{-1}$, (c) the position of the PL peak, unit: nm, and (d) the PL intensity. We can find negligible variation in the frequency of the A1g peak and in the PL intensity.

It is worthwhile to point out that the PL efficiency of the as-grown monolayers vary substantially (by up to one order of magnitude) among different samples or even in the same flake (Fig. 5.3), while the PL of the transferred monolayers is much more uniform (Fig. 5.4). Without losing generality, the PL efficiency of the as-grown monolayers was obtained from the flakes with relatively high PL intensities. The following characterizations were performed on the same set of samples if at all possible.
5.3 Doping effect from substrate-borne moisture

To understand the improved PL efficiency of the suspended monolayers, it is necessary to examine how the transfer process used to prepare the suspended monolayers could impact the materials and the PL. As a matter of fact, the transfer process is very mild with no heat, corrosive chemicals, and capillary forces involved and has been previously demonstrated able to preserve the crystalline quality of the monolayers[127]. The preservation of the crystalline quality is also supported by the uniform, strong luminescence at the suspended monolayers (Fig. 5.1b) as well as by the similar Raman intensity and width at the monolayers before and after the transfer (Fig. 5.5). Additionally, we confirm that the chemicals involved in the transfer process, including polystyrene, solvent (toluene), and water, may be removed by the mild baking (200-300°C under Ar for 30 minutes) in the transfer process and thus have only minor effects on the PL (Fig. 5.6).

![Raman spectra](image)

**Figure 5.5.** Effect of the transfer process on the crystalline quality of the monolayer. Raman spectra of as-grown monolayer MoS2 on sapphire substrates (blue) and the monolayer MoS2 transferred onto another sapphire substrate after the growth (red). The Raman peaks are labeled as shown. We can find no change in the Raman intensity after the transfer. The redshift of the A1g peak indicates increase of n-doping after the transfer.
Figure 5.6. Effect of the transfer process on the PL efficiency. (a) PL of as-grown monolayer MoS2 on sapphire substrates and the as-grown monolayer after treated by polystyrene (PS) and the solvent (toluene). We spin coat a layer of PS (solved in soluene) on top of as-grown monolayer MoS2 on sapphire substrates, and then rinsed it with toluene to remove the polymer for several times. After the rinse we baked the monolayer at 200°C under Ar for 1 hour. All the steps are exactly the same as what used for the transfer process except not involving the lift-off step. We monitored the PL intensity of the monolayer before and after the treatment. (b) PL of as-grown monolayer MoS2 on sapphire substrates and the as-grown monolayer after treated by water. We cast a water droplet on top of as-grown monolayer MoS2 on sapphire substrates and then dried it by annealing at 200°C under Ar for 1 hour. We monitored the PL intensity of the monolayer before and after the treatment.

As further evidence for the minor effect of the transfer process, the monolayer transferred using this wet process shows similar PL efficiency as those transferred by a dry process that involves no chemicals as discussed later (see Fig. 5.7d). Therefore, we can exclude out the transfer process as the reason for the improved PL efficiency in the suspended monolayer. The substrate is what causes the difference in PL between the supported and suspended monolayers. We find that even a trace amount of moisture at the substrate surface may
substantially lower the PL efficiency of MoS$_2$ and WS$_2$ monolayers by n-doping the monolayers. This is evidenced by one order of magnitude lower PL intensities at the transferred MoS$_2$ and WS$_2$ monolayers than the as-grown monolayers on the same substrates (Fig. 5.7a-b).

**Figure 5.7.** Effect of trapped water moisture on the PL efficiency of monolayer MoS$_2$ and WS$_2$. (a) PL spectra of as-grown monolayer MoS$_2$ on sapphire substrates (red curve), the monolayer MoS$_2$ transferred onto another sapphire substrate (black curve) and Teflon substrates (blue curve). (b) PL spectra of as-grown monolayer WS$_2$ on sapphire substrates (red curve), the monolayer WS$_2$ transferred onto another sapphire substrate (black curve) and Teflon substrates (blue curve). The PL spectra in (a) and (b) are normalized with respect to the Raman intensity in order to remove the effect of local field enhancements. More specifically, the PL of the monolayers on Teflon substrates is scaled down by a factor of 1.6 due to the local field enhancement caused the small refractive index of the substrate. (c) PL spectra of the monolayer MoS$_2$ transferred onto scotch tapes using the wet process and a dry transfer (directly applying the tape to the as-grown monolayers and then mechanically peeling it off). (d) PL spectra of the monolayer MoS$_2$ transferred using the wet process and a monolayer MoS$_2$ exfoliated from single crystalline bulk materials onto SiO$_2$/Si substrates. The PL of the transferred monolayers is also broader and redshifts compared to those of the as-grown ones. Similar weaker, broader, and redshifted PL can be generally found at the
monolayers transferred onto many other substrates including SiO$_2$/Si (Fig. 5.1), ITO glass, GaN, quartz, LaAlO$_3$, SrTiO$_3$, and SiO$_2$/Si functionalized with (3-Aminopropyl) trimethoxysilane (APTMS) (Fig. 5.8).

**Figure 5.8.** Heavy n-doping in the monolayer transferred onto hydrophilic substrates. PL spectra of the monolayer MoS$_2$ transferred onto different hydrophilic substrates, including quartz, ITO glass, LaAlO$_3$, and SiO$_2$/Si functionalized with a self-assembled monolayer of (3- Aminopropyl) trimethoxysilane (APTMS) molecules. The PL of as-grown MoS$_2$ on sapphire substrates is also given as a reference. The PL spectra of all the transferred monolayers are multiplied by a constant of 5 for visual convenience.

These features indicate that the MoS$_2$ and WS$_2$ monolayers transferred onto those substrates are heavily n-doped, which has been known able to enable trion-dominated emission featuring with lower efficiencies, broader peaks, and longer wavelengths than the exciton emission[25, 129, 130]. The n-doping is further supported by the substantial redshift of the A$_{1g}$ peak, which indicates the concentration of electrons[131], after the transfer process (Fig.
5.5). However, the heavy n-doping effect may be only found at the transferred monolayers but not the as-grown and suspended monolayers (Fig. 5.1). It is also absent from the monolayers transferred onto hydrophobic substrates such as Teflon and SiO$_2$/Si functionalized with octadecyltrichlorosilane (OTS) (Fig. 5.7 and Fig. 5.9).

**Figure 5.9.** Absence of heavy n-doping in the monolayer transferred onto hydrophobic substrates. PL spectra of the monolayer MoS$_2$ transferred onto different hydrophobic substrates, including polystyrene (PS), polydimethylsiloxane (PDMS), and SiO$_2$/Si functionalized with a self-assembled monolayer of octadecyltrichlorosilane (OTS) molecules. The PL of as-grown MoS$_2$ on sapphire substrates is also given as a reference.

These strongly suggest that the observed heavy n-doping is contributed by water moisture, more specifically, by the water moisture trapped between the monolayer and the substrate as the water on top of the monolayer can be readily removed during the baking process (Fig. 5.6). It has been previously demonstrated that the water moisture trapped underneath may strongly n-dope MoS$_2$ monolayers[132, 133]. Note that the monolayers transferred onto layered materials substrates such as mica with high hydrophilicity also show no sign of heavy
doping, as evidenced by comparable PL in the monolayers transferred and directly grown onto the same layered materials substrates (Fig. 5.10).

**Figure 5.10.** PL spectra of the monolayer MoS2 directly grown on mica substrates and the monolayer transferred onto mica substrates. The transferred monolayer was grown on sapphire substrates first, but we have confirmed no difference in quality for the monolayers grown on the two substrates using Raman measurement. This result indicates negligible difference in the doping for the as-grown and transferred monolayers on mica substrates.

This is because the moisture adsorbed onto layered materials substrates, which may bear a less amount of surface defects, is easier to remove during the baking process than those adsorbed onto conventional substrates. We do find a gradual decrease, broadening, and redshift in the PL of the monolayer transferred onto mica when exposed to ambient environment as mica may attract moisture from the environment.

The trapped moisture can be mainly correlated to the trace moisture that the substrate intrinsically attracts from ambient environment, instead of being introduced by the transfer
process. Should the water moisture result from the transfer process, we would expect similar heavy n-doping in all the transferred monolayers. The monolayer transferred by using this wet process shows similar PL efficiency to those transferred by a dry process that involves no water (Fig. 5.7). And the PL of the monolayers transferred on SiO₂/Si substrates using the wet transfer is very similar to the PL of the monolayer mechanically exfoliated from bulk single crystalline onto the same substrates (Fig. 5.7d). It is worthwhile to point out that the PL of our exfoliated monolayers is consistent with the results in references, which often show trion-dominated emission in the mechanically exfoliated MoS₂ and WS₂ monolayers on SiO₂/Si substrates[1, 25, 114, 116, 117, 134, 135]. All these results support that the transfer process is not the main source of the trapped moisture. Very interestingly, the doping effect of the trapped moisture is negligible for WSe₂. The as-grown and transferred monolayer WSe₂ on SiO₂/Si substrates shows similar PL efficiencies (Fig. 5.2), which is different from what observed at MoS₂ and WS₂ monolayers and indicates much less doping effect of the trapped water moisture to WSe₂.

5.4 Doping effect from substrate charge transfer

Except the doping from substrate-borne water moistures, the substrate itself may dope the monolayer and thereby affect the PL. We investigated the PL of the monolayers supported onto a wide variety of substrates where the effect of trapped moistures is minimal. For simplicity, we mainly focus on monolayer MoS₂, including as-grown monolayer MoS₂ on sapphire and the MoS₂ monolayers transferred onto organic materials or 2D materials substrates. Fig. 5.11 shows the PL of the monolayer MoS₂ on different substrates (see Fig. 5.9 for more results), in which the PL of the suspended MoS₂ is also given as a reference.
Mica substrates may enable the strongest PL at the monolayer among all the substrates we studied, around 2-3 times higher than sapphire substrates, while polystyrene substrates are the worst (Fig. 5.11 and Fig. 5.9). Hexagonal boron nitride (h-BN), which has been reported to be a good substrate for monolayer electronic devices[136], is not as good as mica in terms of promoting the PL in MoS₂. We can exclude out any substantial effect of strains, which was reported able to affect the PL efficiency of monolayers[116, 118, 130, 137-141], in the substrate-dependent PL efficiencies. Only negligible difference (< 0.3%) in strain can be found in the monolayers as indicated by a minor difference in the frequency of the $E_{2g}^1$ peak, which is known sensitive to strain (Fig. 5.11b)[137, 138, 142].
Figure 5.11. Doping effect of the substrate. (a) PL spectra of as-grown monolayers MoS$_2$ on sapphire substrates (red) and the monolayer transferred onto mica (black), h-BN (grey), and Teflon (orange), and polystyrene (blue) substrates. The PL of suspended monolayer MoS$_2$ with the intensity scaled by a factor of 0.03 is also given. The PL of the monolayers on Teflon substrates is scaled down by a factor of 1.6 due to the local field enhancement caused the small refractive index of the substrate. (b) Raman spectra of monolayers MoS$_2$ on different substrates. The two dashed lines indicate the $E^{1}_{2g}$ and $A^{1}_{1g}$ peaks of the as-grown monolayer. (c) Calculated charge transfer between monolayer MoS$_2$ and mica substrate, which shows plane-averaged differential charge density $\Delta \rho$ (red line) and amount of transferred charge $\Delta Q$ (blue line) as a function of the distance in the vertical direction. Also shown is a sideview of the atomic model used in the DFT calculation and the isosurface of charge transfer where green (orange) color denotes diminishing (accumulation) of electrons. (d) Transient differential reflection collected from as-grown monolayer MoS$_2$ on sapphire substrates and the monolayer transferred onto mica, Teflon, and h-BN substrates. The measurement for the monolayer on PS is very difficult due to the thermal instability of PS.
The substrate dependence of the PL efficiencies as shown in Fig. 5.11a and Fig. 5.9 can be mainly ascribed to substrate-induced doping. The higher PL efficiency of the supported monolayer is accompanied with blueshifts of the $A_{1g}$ Raman peak, which indicates the decrease of n-doping level (Fig. 5.11b)[131]. The substrate-induced doping is also supported by the different ratios of trion/exciton emission in the monolayers. We can evaluate the ratio of trion and exciton emissions by numerically fitting the PL spectra (Fig. 5.12).

![Figure 5.12.](image)

**Figure 5.12.** Fitting of the PL emission of monolayer MoS2 on different substrates. The measured PL spectra (red curves) are fitted as a combination of neutral $A$ exciton, trion $A^{-}$, and $B$ exciton emission, each of which is fitted by Lorentzial functions.

The fitting result shows that the higher PL efficiency comes with a lower ratio of trion emission (Table 1). For instance, the monolayer on mica substrates shows the lowest ratio of trion emission. Additionally, we simulated the charge transfer between the monolayer and the substrates using DFT techniques (Fig. 5.11c and Fig. 5.13).
Figure 5.13. Charge transfers between monolayer MoS$_2$ and various substrates. Calculated plane-averaged differential charge density $\Delta \rho$ (red line) and amount of transferred charge $\Delta Q$ (blue line) as a function of the distance in the vertical direction for the monolayer MoS2 on top of different substrates, including (a) Teflon, (b) mica, (c) h-BN, (d) PDMS, (e) sapphire, (f) GaN, and (g) fused quartz. The horizontal dashed line in each plot corresponds to the location of the maximum of the curve at the interface of the adsorbate and the surface and its corresponding value of the gives the transferred charge from the substrate to MoS$_2$. Accompanying with each calculation also shows the topview (bottom) and sideview (right side) of the model structures use in the DFT calculations.
The simulation result confirms that mica can provide the best capability to attract electrons (p-doping) from monolayer MoS$_2$ while polystyrene provides strong n-doping (Table 2). We also studied the PL of monolayer MoS$_2$ directly grown on substrates including mica, sapphire, GaN, quartz, and SiO$_2$/Si (Fig. 5.14-Fig. 5.15), in which the effect of trapped moisture can be ignored as well due to the high-temperature treatment of the substrate in the synthetic process. While larger substrate-induced strains (up to 1.4%) could be found in the as-grown monolayers, the main conclusions, including the important role of substrate-induced doping and the best capability of mica to promote the PL efficiency, hold for the as-grown MoS$_2$ monolayers on different substrates.
Figure 5.14. PL and Raman of the monolayer MoS2 grown on different substrates. (a) PL spectra (b) Raman spectra of the monolayer MoS2 directly grown on different substrates, including mica, sapphire, GaN, quartz, and SiO2/Si. The dashed lines indicate the two Raman peaks in the as-grown monolayer MoS2 on sapphire substrates. The PL is normalized to their corresponding Raman intensities in order to eliminate the effect of local field enhancement. Generally, the monolayers on sapphire, GaN, mica, and quartz substrates show similar Raman intensities, while the monolayer on SiO2/Si (90 nm thermally grown oxide) shows Raman intensity 10 times larger. The Raman measurement indicates a tensile strain of 1.4% in the monolayer grown on quartz substrates, which is expected able to cause 50% decrease in the PL.
Figure 5.15. Comparable crystalline quality in the monolayer MoS2 grown on different substrates. For the convenience of comparison, we grew the monolayers on different substrates (including sapphire, GaN, and quartz) and then transfer them onto the same SiO2/Si substrates for Raman and PL measurements. (a) Raman spectra and (b) PL spectra of the monolayer MoS2 transferred onto SiO2/Si substrates. The similar Raman and PL spectra indicate that the monolayer MoS2 grown on different substrates have similar crystalline quality.

Figure 5.16. Substrate-dependent PL of supported monolayer WS2. PL spectra of as-grown monolayers WS2 on sapphire substrates (red curve) and the monolayer transferred onto mica (black curve), h-BN (yellow curve), and Teflon (green curve) substrates. Also given is the PL spectrum of the as-grown WS2 on SiO2/Si substrates (dark red curve). All the PL spectra are normalized with respect to corresponding Raman intensities in order to eliminate the effect of local field enhancements. We can find that the dependence on the substrate is similar to what observed at the supported monolayer MoS2. Mica may enable an improvement of 2.5 times in PL efficiency compared that of the as-grown one.
Similar effect of substrate-induced doping can be found at monolayer WS\textsubscript{2} (Fig. 5.16), where the p-doping substrate like mica can best promote the PL. However, the PL in monolayer WSe\textsubscript{2} can be best promoted by the n-doping substrate such as polystyrene and h-BN, and is weaker on p-doping substrates (Fig. 5.17).

![Figure 5.17. Raman and PL of monolayer WSe\textsubscript{2} on different substrates. (a) Raman spectra (b) PL spectra of the monolayer WSe\textsubscript{2} transferred onto different substrates, including mica, sapphire, PS, Teflon, and h-BN. The monolayer WSe\textsubscript{2} was originally grown on sapphire substrates. All the PL spectra are normalized to their corresponding Raman intensities in order to eliminate the effect of local field enhancements. The DFT calculation indicates that the charge transfer between monolayer WSe\textsubscript{2} and these substrates is 0.072, 0.004, 0.002, -0.0051, -0.0048 for the substrate of mica, sapphire, Teflon, h-BN, and polystyrene, respectively, where a positive values means p-doping while negative value n-doping.](image)

This is rooted in the different intrinsic doping of the monolayers, as the CVD-grown WS\textsubscript{2} and MoS\textsubscript{2} are known intrinsically n-doped while the monolayer WSe\textsubscript{2} intrinsically p-doped.
The different effects of the same substrate to the monolayers with different intrinsic doping further support the important role of substrate-induced doping in the PL efficiency. The results given in Fig. 5.7 and Fig. 5.11 indicate that the doping effect of the substrate is far weaker than that of the substrate-borne moisture. This is consistent with previous studies that show strong doping to the monolayers from molecular dopants[134, 143, 144]. To better understand the doping effect on the PL efficiency, we investigated the exciton dynamics of the supported monolayers using pump-probing techniques (Fig. 5.11d). What we measured is the differential reflection $\Delta R/R$ of a delayed probe beam from the monolayers after photoexcitation by a pump beam (590 nm), whose amplitude can be correlated to the concentration of photoexcited charges (see Method). While more studies could be necessary, our measurement result nevertheless indicates reasonably similar exciton lifetime with minor variations in the supported monolayers (Fig. 5.11d). This suggests that the different PL efficiencies caused by the substrate-induced doping may essentially result from different radiative lifetimes, the longer radiative lifetime, the lower PL efficiency. A recent study predicts that trions, whose population varies with the doping, indeed have radiative lifetime longer than excitons[145].
5.5 Effect of substrate-defect assisted non-radiative recombination

The doping effect alone cannot account for the dramatic difference in PL efficiencies between the suspended and supported monolayers. In fact, the suspended MoS$_2$ monolayer exhibits similar line width and ratio of exciton/trion emission as that of the mica-supported MoS$_2$ monolayer (Fig. 5.11a and Table 2), suggesting a similar doping level, but its PL efficiency is one order of magnitude higher. We find that the other significant effect of the substrate lies in shortening the exciton lifetime. Fig. 5.19 shows the measured exciton dynamics at the suspended and as-grown monolayers. We have confirmed no substantial heating effect in both suspended and supported monolayers by ensuring a linear dependence of the $\Delta R/R$ at the zero second delay on the pumping fluence (Fig. 4.6 in Chapter 4). Upon photoexcitation, $\Delta R/R$ arises to its maximum value within $\sim$500fs for all the monolayers (Fig. 5.19), which is consistent with what previously reported[122, 146]. However, the decay of the charge carriers in the suspended monolayers is obviously slower than that in the supported monolayers. This dynamics process is more complicated than what previously reported[122, 147], involving exciton-exciton annihilations.
Figure 5.18. Defect-assisted recombination in as-grown monolayer MoS2. Normalized transient reflection $\Delta R/R$ of the monolayer MoS2 measured (a) at different temperatures, 75K, 150K, 220K, and 295K and (b) using different pumping fluences, 5 $\mu$J/cm$^2$, 12.5 $\mu$J/cm$^2$, and 25 $\mu$J/cm$^2$. The result indicates negligible dependence of the exciton dynamics on the temperature and pumping fluence, suggesting the dominance of defect-assisted recombination as reported previously.

We performed thorough analysis on the exciton dynamics previously in Chapter 4[128], and our analysis indicate that the suspension may cause the exciton lifetime to increase by around 7 times (from 110 ps to 760 ps) for monolayer WS$_2$ and around 20 times (from 50 ps to 1 ns) for monolayer MoS$_2$. We have also confirmed the exciton recombination in the supported MoS$_2$ monolayers is dominated by a defect-assisted mechanism as evidenced by independence of the dynamics on pumping fluence and temperature (Fig. 5.18), which is consistent with what previously reported[108, 147]. The substantial increase in the exciton lifetime at the suspended monolayers indicates that the substrate may facilitate the defect-assisted recombination.
Figure 5.19. Effect of the substrate on exciton dynamics. The transient differential reflection of measured from (a) suspended and as-grown MoS$_2$ monolayers and (b) suspended and as-grown WS$_2$ monolayers. The inset of (a) is to illustrate the result around the zero-second decay, and the inset of (b) lists the radiative and non-radiative lifetimes of suspended WS$_2$ (S-WS$_2$), as-grown WS$_2$ (A-WS$_2$) on sapphire substrates, suspended MoS$_2$ (S-MoS$_2$), and as-grown MoS$_2$ (A-MoS$_2$) on sapphire substrates. (c) The transient differential reflection collected from two different areas p1 and p2 on one single flake as indicated. The p1 is from the central area with low PL while the p2 from the edge area with high PL as indicated in the PL mapping. Inset: PL mapping and optical image of the flake in which the dashed square indicates where the mapping PL was collected from (scale bar, 10 µm). The PL spectra collected from the (d) as-grown and (e) suspended flakes with different sizes (~50 µm and ~8 µm). The inset of (e) shows the optical image of the suspended flakes.

The effect of the substrate on the defect-assisted recombination is dependent on the crystalline quality of the monolayer, in particular, sulfur vacancies. We observed the PL at
the edge stronger than the center area of as-grown WS$_2$ monolayer (Fig. 5.19c) and also the PL at smaller monolayer flakes much stronger than at bigger counterparts (Fig. 5.19d), even though the PL wavelengths are identical, which suggests similar doping levels (Fig. 5.20).

![Normalized PL collected from the two different areas p1 and p2 as indicated Fig. 5.19c of the main text. The PL intensity is different by 14 times.](image)

**Figure 5.20.** Normalized PL collected from the two different areas p1 and p2 as indicated Fig. 5.19c of the main text. The PL intensity is different by 14 times.

The area showing lower PL also exhibits a shorter exciton lifetime, indicating faster defect-assisted exciton recombination (Fig. 5.19c). According to previous studies[148, 149], this PL nonuniformity can be correlated to different concentrations of sulfur vacancies as the center area or larger flakes may carry more sulfur vacancies due to the longer exposure to the high temperature growth environment. However, regardless the huge difference in the PL of as-grown monolayers, the PL efficiency and exciton dynamics of suspended monolayers always show to be similar with only minor variation (Fig.5.19e and Fig. 5.21).
Figure 5.21. Similar exciton dynamics in suspended monolayers with different sizes. Normalized transient reflection $\Delta R/R$ collected from suspend big and small monolayer MoS$_2$ flakes as shown in Fig. 5.19e.

This suggests that the defect-assisted non-radiative recombination in the supported monolayers depends on the interaction of the defects in the monolayer with the substrate, where the defects provide a channel for the substrate to affect the exciton dynamics. Our results also indicate that the non-radiative recombination may be suppressed by decreasing the interactions, either removing the substrate or lowering the number of defects. The observed bigger increase in the exciton lifetime of monolayer MoS$_2$ than WS$_2$ after being suspended (Fig. 5.19a-b) may be ascribed to the higher crystalline quality of monolayer WS$_2$, as it has generally been believed that monolayer WS$_2$ may have less defects than monolayer MoS$_2$. 
5.6 Effect of dielectric environment of substrate on out-coupling efficiency

As the last note, we examine the effect of the dielectric environment created by the substrate on the PL of the monolayer. The dielectric environment may have effect on the local electromagnetic field due to the multiple reflection inside the monolayer as illustrated in Fig. 5.22a.

![Figure 5.22](image)

Figure 5.22. Effect of the substrate on radiative decay. (a) Schematic illustration for the interference of radiated light in the monolayers without and with the presence of substrates. Raman spectra of (b) suspended and as-grown MoS$_2$ monolayers and (c) suspended and as-grown WS$_2$ monolayers.

This is evidenced by stronger Raman intensities of the suspended monolayers, ~4-5 times stronger than that of the supported counterparts (Fig. 5.22b-c and Fig. 5.23). The enhancement $Q_{\text{field}}$ of the local field at the suspended monolayer with respect to the supported counterpart can be derived from the Raman enhancement $Q_{\text{Ram}}$ as $Q_{\text{field}} = (Q_{\text{Ram}})^{0.5}$, which is estimated to be around 2-2.2 based on the Raman measurement. This is consistent with our
calculation using the refractive index we measured[150] (Fig. 4.10) and a well-established analytical model and (see S2 in Supplementary Information). The local field enhancement $Q_{\text{field}}$ can lead to an increase in the radiative decay (or decrease in radiative lifetime) of the suspended monolayers.

![Figure 5.23](image)

**Figure 5.23.** Raman spectra of suspended and as-grown WSe2 monolayers on sapphire substrates.

The dielectric environment may also affect the radiative lifetime by providing dielectric screening to change exciton binding energy. Our previous analysis indicates suspending the monolayer may decrease the radiative lifetime by around 2.7-4 times (from 3.7 ns to 1 ns for WS$_2$ and 80 ns to 30 ns for MoS$_2$)[128]. Given the expected decrease of radiative lifetime (by 2-2.2 times) due to the local field enhancement, the effect of the increase of exciton binding energy on the PL efficiency is estimated by a factor no more than 1.4-1.8.
5.7 Conclusion

In conclusion, we demonstrate that substrates can significantly limit the PL efficiency of monolayer TMDC materials, mainly through doping the monolayer and facilitating defect-assisted non-radiative exciton recombinations. The doping may be from substrate-borne moisture and the substrate, the former of which is much stronger than the latter for monolayer MoS$_2$ and WS$_2$ but typically negligible for monolayer WSe$_2$. The doping effect can be substantially mitigated by using proper substrates, more specifically, p-doping substrates like mica for monolayer WS$_2$ and MoS$_2$ and n-doping substrates like h-BN and polystyrene for monolayer WSe$_2$. The defect-assisted recombination depends on the interaction between the defects such as sulfur vacancies in the monolayers and the substrate, and can be suppressed by either removing the substrates or lowering the number of defects. The result may provide very useful guidance for the rational design of high-performance 2D TMDC materials light emission devices. It indicates that organic materials or 2D materials may generally make good substrates for the device development with the monolayers, and that WSe$_2$ may provide a better platform than MoS$_2$ and WS$_2$ due to its less sensitivity to water moisture. Additionally, it indicates that a key strategy to improve the light emission efficiency is eliminating the defect-substrate interaction by either decreasing the number of defects or removing the substrate.
CHAPT 6 : Conclusion

This thesis presents a systematic study of how the strong excitonic effect determines the two main light-matter interaction process in TMDC in both absorption and emission process. For the light absorption process, which indicated by the optical dielectric function of the material, is dominated by the excitonic effect when the layer number of MoS2 film go below than 5. The exciton binding energy is so strong that overturns the band structure effect determines the dielectric function. This conclusion points out a way of largely tuning refractive index electrically. Inspired by this result, we are able to build up a simple field effect device based on monolayer WS2 and realize giant tunability in the refractive index. Besides, we determined other effects of gating field induced charge injections on the monolayer TMDC include: band gap renormalization, exciton binding energy change, electron-exciton scattering rate change and redistribution of exciton and trion transition probability. The fractional dimensional space model has been applied to identify contribution to the tunability of refractive index from each effect. It turns out the interchange transition probability between neutral exciton and trion play the most important role in changing the refractive index. The study on the light absorption/reflection/transmission process of atomically thin TMDC gives more insightful understanding to the fundamental physics. More importantly, it enables us to electrically control the refractive index. This really paves a way to the atomically thin electron-photonic devices. For the light emission process, we studied both intrinsic fundamental limitation and also the external environment effects on the light emission efficiency of monolayer TMDC. We demonstrate the quantum efficiency is limited by the many-body effect, exciton-exciton annihilation for the highly emission efficient suspended TMDC. We also derive a model that gives out the threshold of population
inversion. This provides a very useful guidance for designing laser based on 2D TMDC materials. Other than the intrinsic properties of TMDC, we studied the substrate effect to the light emission efficiency thoroughly. Many substrate effects have been identified: trap moisture doping effect, substrate charge transfer effect, substrate-defects assisted non-radiative recombination and substrate effect on out-coupling efficiency. The conclusion is that the moisture doping effect and substrate-defect assist recombination contribute most in quenching the light emission efficiency. So hydrophobic substrates or suspended structure are proposed in order to enhance the light emission efficiency in practical applications.

The 2D TMDC is a very promising candidate in application of nanophotonics. This thesis has solved some fundamental problems of understanding and engineering the light-matter interaction of TMDC. Based on the studies, in the future, electrical control photonic device base on TMDC are possible, like optical modulator and light steering meta-surface. Highly efficiency TMDC LED and Laser can also be realized by carefully engineering the environment. Also, the extremely strong many-body interaction of this material may also generate new physical phenomena wait for discovery.
PUBLICATIONS FOR YILING YU

Publications covered in this thesis


2. Yifei Yu§, Yiling Yu§, Chao Xu§, Yong-qing Cai, Liqin Su, Yong Zhang, Yong-Wei Zhang, Kenan Gundogdu, Linyou Cao, Engineering Substrate Interactions for High Luminescence Efficiency of Transition Metal Dichalcogenide Monolayers, Adv. Fun. Mat. doi:10.1002/adfm.201600418 (§ equally contribution authors)

3. Yiling Yu§, Yifei Yu§, Chao Xu§, Andy Barrette, Kenan Gundogdu, Linyou Cao, Fundamental Limits of Exciton-Exciton Annihilation for Light Emission in Transition Metal Dichalcogenide Monolayers. Physics Review B: Rapid Communication 93 (20) 21111 (§ equally contribution authors)

4. Yiling Yu, Yifei Yu, Lujun Huang, Haowei Peng, John Perdew, and Linyou Cao, Gating Refractive Index of Transition Metal Dichalcogenide Monolayers (to be published)

Publications not covered in this thesis


6. Yiling Yu and Linyou Cao, Coupled leaky mode theory for light absorption in 2D, 1D, and 0D semiconductor nanostructures, Optics Express 20, 13847-13856, (2012)


13. Lujun Huang, Guoqing Li, Alper Gurarslan, Yiling Yu, Ronny Kirste, Wei Guo, Junjie Zhao, Ramon Collazo, Greg Parson, Michael Kudnov, and Linyou Cao, Atomically Thin Narrowband and Broadband Light Superabsorbers (Accepted by ACS Nano)

14. Alper Gurarslan, Shuping Jiao, Taide Li, Guoqing Li, Yiling Yu, Yang Gao, Elisa Riedo, Zhiping Xu, Linyou Cao, Van der Waals Force Isolation of Monolayer MoS2 (to be published)
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