Tunable Emission from Two-dimensional Semiconductor with Platelet Optical Antennas

by

Yingyi Yang

Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 2015

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Abstract

The remarkable properties of two-dimensional semiconductors allow for abundant research and applications in electronic and optoelectronic area. Monolayer transition metal dichalcogenides (TMDC), such as MoS$_2$, are direct bandgap semiconductors which hold promises in valley-based optoelectronic applications or light-emitting devices. However, the weak light-matter interaction in this atomically thin slab leads to low absorbance ($\sim 3\%$) and quantum yield ($\sim 10^{-3}$). Although the quantum yield of monolayer MoS$_2$ is higher compared with its few-layer counterparts, it is still significantly lower than that would be expected for a direct-gap semiconductor. Here, we explore the possibility of tuning the spontaneous emission of monolayer MoS$_2$ by coupling it with plasmonic platelet antennas, which can both convert freely propagating light into nanoscale and transmit radiation power into free space efficiently. The antennas used are single crystalline and the plasmonic modes are obtained both by near-field imaging and numerical simulation. The tunability of photoluminescence by nearby antenna is analyzed in details. This thesis proposes an economic and promising way to tune the emission of low-quantum-yield emitters, such as MoS$_2$, while preserving both A and B exciton peaks. This ultrathin structure can facilitate the development of on-chip emitters and valley-based devices.

Thesis Supervisor: Nicholas X. Fang
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Acknowledgments

I would like to sincerely express my gratitude to Professor Nicholas X. Fang for his inspiration and support in my research and academic study during the past two years at MIT. His patient guidance was important for the development of my project. I would also like to thank Matt Klug, who initiated the synthesis of platelet antennas and introduced chemical bench work to me, Anshuman Kumar, who helped me with physical concepts and offered suggestions at critical moments, Yoon Kyung (Eunnie) Lee, who helped me with simulations and shared her positivity. I thank Steven Kooi and William DiNatale at ISN for their help in the experimental setup, and Dr. Dafei Jin, who tested my samples in our collaborator’s lab. I would also like to thank Chu Ma and Zheng Jie Tan, who shared the moments of happiness and hardships, and Dr. Jun Xu, Dr. Qing Hu, Dr. Sam Hoon Nam, for their help in the lab. Apart from the names mentioned above, I am thankful to visiting professor Xiang Xiong, who shared his knowledge in optics and his optimism towards life.

This work is made possible through the financial support by the NSF (grant CMMI-1120724) and AFOSR MURI (Award No. FA9550-12-1-0488).
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Chapter 1

Introduction

1.1 Motivation

1.1.1 Emerging optoelectronic applications of two-dimensional semiconductors

The remarkable properties of two-dimensional materials—flexibility, transparency, strength—allow for abundant research and applications in electronic and optoelectronic area [1, 2, 3]. Transition metal dichalcogenides (TMDCs) are layered materials with strong intralayer bonding and weak interlayer bonding, which enables them to be exfoliated into two-dimensional layer with thickness on the order of a single atom [4]. Compared with graphene, TMDCs such as MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$ have band gaps that change from indirect to direct in monolayer [5], providing significant advantages in optoelectronic applications including photodetectors, sensors, photovoltaic and light-emitting devices [6, 7, 8, 9, 10, 11, 12, 13, 14]. Flexible optoelectronic devices holds promise in wearable electronics and transparent displays [7, 15, 16, 17]. The flexibility also results in the tunability of bandgap [18, 19, 20]. Their ability to absorb and emit light is directly affected by their electronic band structure. For direct bandgap semiconductor, they can readily absorb photons with energy greater than the bandgap energy, and emit photons with energy corresponding the the bandgap. On the other hand, the absorption and emission should be assisted by phonon in indirect bandgap
semiconductor, because extra momentum is needed for optical transition in different valleys. In terms of MoS$_2$, the crossover from indirect to direct bandgap is observed in changes in absorption and photoluminescence [21, 22, 23]. This shift leads to $10^4$ times increase in the quantum yield [22].

Figure 1-1: Atomic representation of TMDC structure. (a) Schematic representation of typical TMDC structure (b) Atomic structure of hexagonal symmetry from Ref [2]

Figure 1-2: Simplified electronic band structure for MoS$_2$ from Ref [22]

Their direct bandgap in the visible range makes TMDCs attractive as the light-absorber in photovoltaic devices and photodetector [24, 11]. The conduction and valence-band edges of several TMDCs are compatible with typical electrodes, so the
electrons can transport across the Schottky barrier in the heterojunction under biased voltage [2].

Figure 1-3: An ultrasensitive monolayer MoS$_2$ photodetector. (a) Schematic view of monolayer MoS$_2$ photodetector (b) Time-resolved photoresponse of the device from Ref [11]

An ultrasensitive monolayer MoS$_2$ photodetector with high photoresponsibility is shown in Figure 1-3 [11]. When the device is illuminated by photons with energy larger than the bandgap, the light is absorbed and electron-hole pairs are thus generated. They can be extracted by applying a drain-source bias, resulting in the formation of photocurrent. The device shows high photoresponsibility because of the direct bandgap, and low dark current due to the presence of the bandgap. In addition, photodetection of different wavelengths, i.e. detection of green light with single- or double-layer, and detection of red light with trilayer, can be achieved by using MoS$_2$ of different layers [8].

Electroluminescence (EL) and photoluminescence (PL) are two important applications of MoS$_2$ [25, 21]. Photons are emitted in response to electrical field in EL. This mode works in light-emitting diode (LED). On the other hand, photons, typically of higher energy, are absorbed and re-emitted in PL. Similarly, the direct bandgap of monolayer MoS$_2$ makes it an ideal candidate as active light-emitting layer. A monolayer MoS$_2$ LED with a vertical p-n junction has been demonstrated in Figure 1-4 [26]. The heterostructure composes of n-type MoS$_2$ and p-type silicon, with the former serving as electron injection layer and the latter serving as hole injection layer.
The electron-hole pairs can radiatively recombine in the junction under forward bias. The presence of A\textsuperscript{−} peak originates from the tightly bond trions in MoS\textsubscript{2} [27]. This heterojunction diode can also operate as photovoltaic device, in which the process is reversed in that light is absorbed and photocurrent is generated.

An interesting property of TMDCs such as MoS\textsubscript{2} is their spin, orbit and valley interactions [28, 29, 30, 31]. Monolayer MoS\textsubscript{2} belongs to D\textsubscript{3h} point group which lacks inversion symmetry as can be seen from its atomic structure in Figure 1-5, while bilayer MoS\textsubscript{2} is centrosymmetric [32]. This leads to a strong spin-orbital splitting of valence band maximum at K valley, and the resulting two PL peaks are called A and B excitons. Moreover, the spin degeneracy is lifted at the band edge. Therefore, A exciton can be selectively excited under circularly polarized light, which provides the additional momentum needed to satisfy the optical selection rule [28, 29]. This effect is stable thanks to the large spin-orbital interaction, which is quite distinctive in TMDCs and may lead to many promising applications, such as transistor [33, 34].

1.1.2 Weak light-matter interaction in two-dimensional semiconductors

In the previous section, TMDCs are shown to be promising candidates in optoelectronic applications. However, for optoelectronics and photonics applications, light-matter interaction is a critical issue because the typical interaction length is smaller
than the wavelength of light. Atomically thin nature of monolayer thickness poses a challenge due to the weak light-matter interaction [35]. From the reported experimental results in Figure 1-6, we can that both absorption [27] and quantum yield [22] are poor in monolayer MoS₂ slab.

The absorbance normalized by the number of thickness shows that monolayer MoS₂ has quite low absorption. This is intuitive due to the imaginary part of refractive
index, which leads to the exponential decay of field in MoS$_2$. On the other hand, although the quantum yield of monolayer MoS$_2$ is higher compared with its few-layer counterparts, it is still significantly lower, i.e. up to $10^{-3}$, than that would be expected for a direct-gap semiconductor. It should be mentioned that the quantum yield can be improved if the sample is suspended or transferred onto hBN flakes [28].

Given this inherent drawback in this atomically thin slab, I use optical antennas to boost the light-matter interaction. They are widely used to enhance the photoemission of the nearby emitters [36, 37, 38, 39, 40, 41, 42, 43]. These antennas can convert freely propagating electromagnetic waves into localized energy, typically on nanometer scale [44, 45, 46], which is compatible with the thickness of MoS$_2$ flakes. Furthermore, they can also serve as transmitters to direct the radiative wave [47, 48]. In general, these antennas achieve the manipulation of optical field in a nanometer scale. Nobel-metal nanostructures can serve as antennas in the visible range due to the collective oscillation of electrons in the conduction band in resonance with optical field [49]. Among all types of metallic nanostructures, I use silver nanoplates as antennas because of the following reasons: First, the resonance frequency is readily tunable by changing the lateral size; second, the imaginary part of refractive index is small for silver, resulting in negligible ohmic loss; third, the platelet geometry is compatible with two-dimensional semiconductors.

1.1.3 Wide applications of optical antennas

Light can be focused by dielectric materials, which cannot focus light to area smaller than half of the wavelength. However, optical antennas with feature size on the order of nanometers have many important applications because of the presence of "hotspots". This property holds promise for improving the efficiency of photodetection [50], light emission [51, 52], biological and chemical sensing [53], energy harvesting [54] and spectroscopy [55]. The goal of optical antenna design is to optimize the energy transfer between the localized source and free-space radiation.

In a general antenna problem consisting of a transmitter and a receiver, the antenna can be used to enhance the transmission efficiency, and the antenna efficiency
Figure 1-7: Wide range applications of optical nanoantennas. (a) Germanium photodetector enhanced by dipole antenna [50] (b) Single-molecule fluorescence enhancements by a bowtie nanoantenna [39] (c) Near-field Raman imaging of single-walled carbon nanotubes [55] (d) Unidirectional emission of quantum dot coupled to nanoantenna [47]

can be represented as [44]:

\[ \varepsilon = \frac{P_{\text{rad}}}{P} = \frac{P_{\text{rad}}}{P_{\text{rad}} + P_{\text{loss}}} \]  

(1.1)

where P is the total power dissipated by the antenna, \( P_{\text{rad}} \) is the radiated power and \( P_{\text{loss}} \) is the power dissipated through other channels, such as by absorption of the antenna. Moreover, the transmission can also be improved by directing the power of radiation [44], but this is not the focus of this thesis. Another important antenna parameter is the antenna aperture, which is denoted by the absorption cross-section \( \sigma \):

\[ \sigma = \sigma_o \frac{|E \cdot n_p|^2}{|E_o \cdot n_p|^2} \]  

(1.2)

where \( \sigma_o \) is the cross-section of the dipole-like receiver, \( n_p \) is the unit vector in the direction of the dipole absorption axis, \( E_o \) is the incident field at the receiver and \( E \) is the enhanced field when the receiver couples with the antenna [44]. Take the application of optical antennas in photodetector as an example, the optical antenna
can increase the absorption cross-section and hence the light flux on a detector, contributing to a high signal-to-noise ratio. Furthermore, the absorption depth limits the thickness of the thin-film devices, while optical antennas can be used to reduce the critical dimensions of the devices. This is particularly promising for photovoltaic devices, which can have lower carrier collection length and impurity recombination while keeping the same optical absorption [54].

Generally, optical antennas have become a critical tool in terms of light manipulation at the nanometer scale. In this thesis, I will mainly discuss how to incorporate single crystalline platelet antenna with the emerging 2D semiconductor-MoS$_2$, in order to improve its photoluminescence and give full play to its strength in the application of on-chip compact devices [56].

1.2 Thesis outline

In this thesis, I will discuss about both the experimental results and the theoretical calculation regarding controlling the emission of monolayer MoS$_2$ by optical platelet antennas. The thesis is divided into three chapters. In the first and second chapter, I will discuss the preparation of MoS$_2$ flakes and silver platelet antennas respectively, as well as their optical properties. In the third part, I will build a model to study the coupling between MoS$_2$ and antenna. The theoretical model can also be applied to
other dipole-emitter system to investigate the quenching or enhancement of PL.

1.2.1 Preparation and optical properties of MoS2 flakes

This section demonstrates the micro-mechanical exfoliation of MoS2 flakes. Then the thickness is measured by atomic force microscope (AFM), and the optical properties are measured by Raman spectroscopy and micro-PL. The strong correlation between the layered structure and the evolution of optical properties is discussed in details. Furthermore, I have also tried to transfer MoS2 onto other substrates which may extend the application of MoS2 in optoelectronic field.

1.2.2 Silver single crystalline platelet antennas

In this section, I will document several methods I used to synthesize single crystalline platelet antennas. The advantages and disadvantages of these methods are shown by both extinction spectra and transmission electron microscope (TEM) characterization. The plasmon modes in single crystalline triangular plates are mapped by Electron Energy-Loss Spectroscopy (EELS). In the last subsection, the high-order plasmon modes are generated by Finite-difference time-domain (FDTD) simulation.

1.2.3 Tuning the emission of monolayer MoS2 by platelet antennas

This section aims at obtaining the theoretical PL enhancement in MoS2-antenna system. The emission of MoS2 is controlled by manipulating two processes: excitation and emission. Separating excitation and emission factors has remained a challenge, so their relative contributions are often studied by simulations [43]. I initially have analytically investigated a simple model containing a horizontal dipole and a spherical antenna. This basic scheme gives two pieces of information: first, the enhancement and quenching of PL is governed by the dipole-antenna distance; second, the PL of emitters with lower intrinsic quantum yield have larger potential to be enhanced by the antenna nearby. The excitation rate enhancement is obtained by calculating
the field enhancement at the dipole location, while the quantum yield enhancement is obtained by calculating the rate enhancement of different decay channels. In addition, the tunability of PL is verified by experiments. Finally, some preliminary Time-resolved PL results are also shown.
Chapter 2

Preparation and optical properties of MoS$_2$

2.1 Exfoliation of few-layer MoS$_2$ flakes

Similar to graphene, MoS$_2$ flakes can be obtained by mechanical exfoliation due to the weak interlayer van der Waals force [4]. The bulk MoS$_2$ is bought from SPI, and the scotch tape is from 3M. The exfoliated MoS$_2$ flakes are transferred onto a silicon oxide substrate, which is cleaned with Piranha solution and rinsed with IPA and then blow dried with N2. Here 300nm silicon thermal oxide wafer is used because it could provide relatively good optical contrast. This can be confirmed by considering the interference in a trilayer stack and normal incidence in Figure 2-1.

![Figure 2-1: Trilayer stack for better optical contrast](image)

The reflectance is [57, 58]
\[ R = \left| \frac{r_1e^{i(\phi_1+\phi_2)} + r_2e^{-i(\phi_1-\phi_2)} + r_3e^{-i(\phi_1+\phi_2)} + r_1r_2r_3e^{i(\phi_1-\phi_2)}}{e^{i(\phi_1+\phi_2)} + r_1r_2e^{-i(\phi_1-\phi_2)} + r_1r_3e^{-i(\phi_1+\phi_2)} + r_2r_3e^{i(\phi_1-\phi_2)}} \right|^2 \]  

(2.1)

where \( \phi_1 = \frac{2\pi}{\lambda} n_1 d_1 \) and \( \phi_2 = \frac{2\pi}{\lambda} n_2 d_2 \) are optical path difference in MoS\(_2\) and SiO\(_2\) layers. Since we compare the regions with and without MoS\(_2\) flakes, the contrast can be defined as

\[ C = \frac{R(n_1 = 1) - R(n_1)}{R(n_1 = 1)} \]  

(2.2)

The contrast versus illumination wavelength and SiO\(_2\) thickness is given in Figure 2-2.

![Optical contrast of the trilayer stack.](image)

**Figure 2-2:** Optical contrast of the trilayer stack. (a) Contrast versus illumination wavelength and SiO\(_2\) thickness (b) Contrast at 550nm illumination

Under white light illumination, it is reasonable to choose 300nm silicon oxide substrate because 550nm wavelength is most sensitive to human eyes. Figure 2-3 shows one representative optical microscopy image.

Based on this figure, the number of MoS\(_2\) layers can be estimated. The light blue region most likely corresponds to monolayer, while the whiter regions correspond to few-layer flakes [59].

The thickness of MoS\(_2\) is further confirmed by atomic force microscopy (AFM) working under tapping mode. Under tapping mode, there is attractive force between the tip and the sample. Here the AFM is Dimension 3000 in ISN at MIT. Since the
thickness of monolayer MoS$_2$ is typically under 1nm, laser alignment is important. The motion of the tip is adjusted delicately by a feedback loop. The height information is recorded by the color scale in Figure 2-4. The background noise has been removed by low pass filtering.

The height profile shows that monolayer MoS$_2$ is around 0.8nm, which agrees well with literature [59, 21].

Large-area MoS$_2$ can be grown by Chemical vapor deposition (CVD) [60, 61, 62],
which greatly improves the yield of high-quality monolayer samples.

2.2 Optical properties of MoS$_2$

The optical properties of MoS$_2$ attract much attention not only because it has direct band gap in the visible range, but also arise from its relatively large spin-orbital splitting in the valence band maximum [32]. Figure 2-5 is the calculated layer-dependent band structure of MoS$_2$ [21]. The smallest energy transition is indicated by the arrow. Bulk MoS$_2$ has an indirect bandgap. The direct transition at K valley has higher energy in few-layer MoS$_2$. With the reduced layer thickness, the direct transition almost shows no change while the indirect bandgap becomes larger.

![Figure 2-5: Band structure of MoS$_2$ from [21]. (a) Bulk MoS$_2$ (b) Quadrilayer MoS$_2$ (c) Bilayer MoS$_2$ (d) Monolayer MoS$_2$.](image)

Confocal Raman spectroscopy is used to characterize the optical properties of MoS$_2$ flakes. The setup shown in Figure 2-6 is Horiba LabRAM with 532nm excitation laser. The pinhole aperture in front of the light source greatly reduces the laser spot size on the sample. The size of the pinhole can be adjust accordingly. Another pinhole aperture between the objective lens and the image plane rejects the rays from out-of-focus points on the sample and works as a spatial filter. Both Raman and photoluminescence (PL) signals can be detected by this setup. They correspond
to different frequency regions. Raman effect is a form of inelastic light scattering. When the sample is illuminated by the laser, some vibration states will be excited and the sample will be in a virtual energy state. Then the resulting scattered photon can either have lower or higher energy than the incident photon. The former case is designated by Stokes shift, while the latter case is designated as anti-Stokes shift. Such signal is close to the original incoming laser signal because the phonon vibration modes have significantly lower energy compared with photon energy. On the other hand, the PL signal is away from the incoming laser signal.

![Schematic diagram of confocal Raman spectroscopy](http://www.chm.bris.ac.uk/pt/diamond/stuthesis/chapter2.htm)

Figure 2-6: Schematic diagram of confocal Raman spectroscopy (Courtesy from http://www.chm.bris.ac.uk/pt/diamond/stuthesis/chapter2.htm)

Figure 2-7 and 2-8 show the PL curves corresponding to different layers of MoS₂. It is clear that few-layer MoS₂ has three peaks. They are A exciton, B exciton and indirect transition [22]. A and B excitons are direction transitions from conduction band to the valence band at K valley. The indirect transition shows a blue shift when the number of MoS₂ layers decreases [21]. Hence, for monolayer MoS₂, the indirect transition gap is larger than direct transition gap, and MoS₂ becomes direct band gap. This makes its emission more efficient, as can be seen from its relatively higher quantum yield [22].

29
Figure 2-7: Crossover from indirect to direct band gap

Figure 2-8: PL curves for MoS$_2$ with different number of layers
The A exciton is at around 670nm, while the B exciton is at around 623nm. So the spin-orbital splitting is about 140meV. For monolayer MoS₂, the indirect transition peak is absent, providing us a way to determine the number of layers [22].

Another reliable way to identify the thickness of MoS₂ is Raman spectroscopy [63], which can characterize the lattice vibration modes in materials. Typically, when the sample is optically excited by laser beam, there will be some certain phonon modes which leads to inelastic scattering. This vibration energy is much lower than electron transition energy, and the corresponding frequency can be determined by measuring the energy difference between incident light and the collected light. This inelastic scattering process will generate Raman shifts, which are like the fingerprint of the material. This can be seen from the Raman spectra of MoS₂ in Figure 2-9.

![Raman spectra of MoS₂](image)

Figure 2-9: Raman spectra of MoS₂

In the phonon spectra, $E_{2g}$ mode corresponds to in-plane lattice vibration, while $A_{1g}$ mode corresponds to out-of-plane vibration. When the number of layers is reduced, the out-of-plane vibration will be weaker due to the decreasing restoring force, which arises from the interlayer van der Waals force. Monolayer sample has in-plane vibration mode at around $385cm^{-1}$, and out-of-plane mode at around $404cm^{-1}$. The
frequency difference of these two modes in Figure 2-10 can also be used to determine the number of layers. For monolayer, the difference is around 18cm$^{-1}$ to 19cm$^{-1}$, according to the literature [63].

![Figure 2-10: Frequency difference identification of number of layers](image)

2.3 Transfer MoS$_2$ onto different substrates

Originally MoS$_2$ flakes are exfoliated onto silicon oxide substrate because it provides better adhesion and contrast. But sometimes we need other substrates, such as hBN, photonics crystal and gold. hBN is used to increase the quantum yield of MoS$_2$ [28], and silver or gold can be used to investigate the coupling between plasmon and MoS$_2$. In this section, I will demonstrate the technique of transferring MoS$_2$ onto gold.

There are many ways to do the transfer. The key point is that we should add a sacrificial layer, which enables MoS$_2$ to detach from the original substrate. One example to combine graphene and hBN flakes is demonstrated in Figure 2-11 [64]. In this paper, graphene is exfoliated onto PMMA layer, which is spin-coated onto a water-soluble layer. After the stake is immersed in the DI water, graphene is detached
from the substrate, and then a new glass slide is used to carry the graphene/PMMA layer.

Figure 2-11: Transfer graphene onto hBN flakes from Ref [64]

Here I use similar method to transfer MoS$_2$ flakes. But since exfoliation MoS$_2$ onto a polymer layer will degrade the contrast and thus add difficulty to the thickness identification, I use the method shown in Figure 2-12.

Figure 2-12: The method I use to transfer MoS$_2$ onto different substrates

In a transferring process, 200nm PMMA is spin-coated onto the MoS$_2$/SiO$_2$/Si stack. Then the sample is immersed into a NaOH bath, and the solution heated at
80 degrees. After around 30min, the SiO$_2$ layer is etched away and the PMMA/MoS$_2$ will float on the solution. Then a new substrate is used to carry PMMA/MoS$_2$, and later PMMA is dissolved by acetone. The optical microscope images in Figure 2-13 show that a certain MoS$_2$ flake is successfully transferred onto gold substrate. We can also see that the color of MoS$_2$ is different when it is on gold substrate, because the change of refractive index affect the optical interference in this multilayer stack.

Figure 2-13: Transfer MoS$_2$ from SiO$_2$/Si onto gold

There are some points we need to concern about in the transfer. Firstly, there should be strong adhesion between MoS$_2$ flakes and PMMA layer, so a post-bake is needed after spin-coating. Secondly, there will be some PMMA residue after rinsing the sample with acetone. One way to remove these residue is to use oxygen plasma etching. In general, this technique works well. I have also tried HF etching, which is not only inefficient but also dangerous. Since MoS$_2$ itself is mechanically flexible, it can be transferred onto other flexible substrates, such as PET and PDMS, which holds promise in flexible display and optoelectronic applications.
Chapter 3

Silver single crystalline platelet antennas

3.1 Synthesis of colloidal silver nanoplates

3.1.1 Why colloidal silver nanoplates

Metallic nanostructures can serve as antennas to convert freely propagating light into localized electric fields with nanometer precision. This arises from the collective oscillation of conduction electrons in the metal nanostructure in resonance with the incident light. With delicate control of the size and shape of the nanostructures, light can be effectively manipulated at nanoscale based on different needs. This is known as localized surface plasmon resonance (LSPR) [49, 65, 66].

Among other metals, i.e. Au, Cu, Li and Al, which can support surface plasmons in the visible and near-infrared regions, silver might be the most important one because it offers many advantages.

A simple way to illustrate LSPR is Mie theory, which deals with the extinction (absorption plus scattering) cross section of the nanostructure:

$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_i}{(\varepsilon_r + 2\varepsilon_m)^2 + \varepsilon_i^2}$$  (3.1)
Figure 3-1: Localized surface plasmon resonance (LSPR). (a) Schematic illustration of LSPR (Courtesy from https://gregemmerich.wordpress.com/2012/11/16/surface-plasmon-resonance-technology-overview-and-practical-applications/) ((b) Enhancement of local field (Simulated by FDTD))

Figure 3-2: Permittivities and quality factors of different metals. (a) Real and imaginary parts of permittivity (b) Quality factor of LSPR for a metal/air interface from Ref [49]
where R is the radius and $\varepsilon_m$ is the dielectric constant of the medium surrounding the nanostructure. The strong resonance condition is satisfied when $\varepsilon_r$ is close to $-2\varepsilon_m$, and $\varepsilon_i$ is close to zero. This is only possible for metal. The dispersion curve of permittivity in Figure 3-2 shows that silver is a good candidate for LSPR thanks to its negative real part of permittivity and small imaginary part of permittivity, which is less lossy compared with gold. Moreover, silver has higher quality factor over a wide spectrum. All these denote that silver has less damping and stronger plasmon resonance. Admittedly, in practical application the material properties should also be taken into consideration. For example, silver can be easily oxidized in the air, so sometimes gold is used for plasmonic applications.

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*Figure 3-3: Summary of the shapes, LSPR absorption peaks, applications and methods for synthesis of Ag nano structures [49]*
Among the rich variety of shapes, i.e. sphere, cube, octahedron, rod, polygonal plates, the platelet shape possesses an extreme degree of anisotropy due to its unique two-dimensional geometry, which provides them with high tunability of localized surface plasmon resonance covering the visible spectrum. Many techniques [67] have been used to investigate the plasmonic excitation in plasmonic nanostructure, such as Electron Energy Loss Spectroscopy (EELS) [68, 69, 70, 71, 72, 73, 74], Cathodeluminescence (CL) [75, 76, 77, 78], Near-field Scanning Optical Microscopy (NSOM) [79] and two-photon photoluminescence (TPPL) [80]. When the information of dark modes and bright modes are obtained by these techniques, their coupling behavior with quantum emitters can thus be retrieved [68]. Compared with samples fabricated by lithographic methods, these colloidal single crystalline nanoparticles have smoother surface and fewer defects, which may otherwise degrade their plasmon resonance quality [44]. In addition, the presence of grain boundaries in amorphous samples is also a drawback when electron beam is used to probe the plasmonic modes. Typical synthesis approaches to produce nanoplates with well-controlled morphologies include polyol process [81, 82], seed-mediated growth [83, 84] and light-induced synthesis [85, 86, 87]. In this section, I will document some chemical synthesis methods I have used to obtain silver nanoplates. The methods are abundant and summarized in Figure 3-3 [49].

3.1.2 Direct reduction and etching

In all the methods I have tried, I use silver nitrate (AgNO₃) as precursor. For typical face-centered cubic (fcc) nobel metal, truncated nanocubes and multiple twinned particles are thermodynamically favored structures. So the kinetic control of reduction process is a key factor in obtaining nanoplates [88].

In a standard synthetic approach, sodium borohydride (NaBH₄) serves as the reducing agent, and sodium citrate serves as the capping agent which preferentially binds to the (111) face. Hydrogen peroxide (H₂O₂) is added as the etchant to dissolve the unstable nanoparticles of other structures. Hence, the remaining silver particles will favor planar growth and form plate structures, as shown in the High-Resolution
Transmission Electron Microscopy (HRTEM) images in Figure 3-4. During the reaction process, poly(vinylpyrrolidone) (PVP, $M_w = 29,000$ g/mol) is added as a stabilizer to reduce the plate size distribution. When NaBH$_4$ is rapidly added into the precursor solution, the solution initially turns light yellow, an indication that spherical particles are formed. With the next several seconds, the solution changes from yellow to red, green and blue. When the ratio of NaBH$_4$ to H$_2$O$_2$ is changed, the resultant color of the solution will also be different. This demonstrates the dynamic equilibrium between the reduction and etching.

Figure 3-4: HRTEM images of silver nanoplates made by direct reduction and etching

Since the reaction process is very fast, it is difficult to control the size of the particles within tolerance. The wide resonance peak in Figure 3-5 indicates the wide size distribution of the particles.

### 3.1.3 Polyol process

In a typical synthesis, a polyol serves as both solvent and reducing agent. At the initial stage of the reduction process, Ag atoms form small clusters of fluctuating structure. After these clusters grow larger, they become more stable and evolves into one of the three predominant structures: single crystalline, single twinned and multiply twinned. Here I modify the protocol in the paper which reduces AgNO$_3$ by the hydroxyl end group of PVP [81]. Since the reduction is substantially slow, the nucleation and growth has been turned into kinetic control, and the final products can deviate from the thermodynamically stable ones. After the reaction is stopped,
the particles are separated from the solution by centrifugation, and then dispersed with ultrasonic dispersion. This process is repeated three times to guarantee that most of the polymer is removed. Then the particle solution is diluted and dropped cast onto the TEM grid. As can be seen from the HRTEM images in Figure 3-6, the size of the triangular plates increases with time.

The yield of the triangular plates is not high, as is shown in the HRTEM images. This situation does not change when I vary the concentration of the reactants. The UV-Vis spectra in Figure 3-7 and 3-8 also show the presence of the spherical particles, which have resonance at around 400nm, regardless of the size of the particle. To obtain a sense of the size and the corresponding resonance of the plate, Lumerical FDTD is used to calculate the extinction cross section of a single triangular particle both in the air and water. The TFSF plane wave source is used. The edge length of the plate is 100nm and the thickness is 12nm. The small peak at around 380 nm corresponds to out-of-plane quadrupole resonance, and the peak at around 420 nm corresponds to in-plane quadrupole resonance. This can be seen by placing a 2D profile monitor perpendicular to the plate. All the resonance peaks will redshift in the water, which agrees with the prediction of Mie theory. In general, this method realizes the size control of the triangular plate.
Figure 3-6: HRTEM images of different reaction time (a) 9h (b) 21h (c) 30h
In order to remove the spherical particles, I have tried two methods. One is by membrane filter, and the other is by centrifugation. But they do not work well. For membrane filter, the particle will stay in the holes and hindering the filtering process. In terms of centrifugation, since the particles to be separated have different weight and shape, it is theoretically possible to separate them by centrifuge. Each time, the precipitation is separated from the solution and then dispersed by ultrasonic dispersion. After many times, the remaining is mostly spherical particles. This method is not so efficient, so I try to improve the yield by modifying the reaction.
process.

Many researchers reported that light can induce the transform of spherical particles to triangular plates by plasmonic excitation [85, 86, 87]. In this process, high-power laser or LED sources with single wavelength is good choice because of its size selectivity. However, since we do not have these light sources, I use broad band and high-power white light source instead. Although it does not have size selectivity, Figure 3-10 indicates that the yield of the triangular plates is improved a little bit.

Hexagonal plates also form during the growth process. This proves the planar growth of the plate. In addition, selected-area electron diffraction (SAED) is implemented by inserting the aperture in the back focal plane. Figure 3-12 can help us
better understand this imaging process. Here the smallest aperture can select 1um area, so a single triangular plate is selected in this area for electron diffraction. When the Bragg’s Law $2dsin\theta = n\lambda$ is satisfied, the electron beam diffracted by a certain set of crystal planes will form constructive interference. Hence, there are corresponding rotationally-symmetric diffraction spots centered around the central point on the back focal plane. All the diffraction pattern belongs to the zeroth order Laue zone. Since the electron beam is normally incident on the sample, the six-fold symmetric diffraction pattern proves that the plate is single crystalline and the upper and lower faces are (111) plane.

The Ag triangular plates synthesized by this method have been used in EELS mapping because of their well-defined shape and large edge length.

3.1.4 Seed-mediated growth

In this subsection, I will document the method I use to grow Ag nanoplates which can meet my needs, i.e. narrow size distribution and with resonance frequency close to the absorption/emission of MoS$_2$.

Unlike the methods discussed in the previous section, the nucleation and growth steps are separated in the seed-mediated growth, allowing for manipulation of the
size and shape of the resultant nanostructures. This method is highly versatile in that both the small variation in the chemical concentration and the mixing speed will affect the shape of final products. Therefore, the concentration of the reactants is kept very low in order to slow down the reaction and bring it under control.

In a typical synthesis process, two steps are involved. In the first step, a suspension of spherical seeds are prepared as follows: silver nitrate (AgNO₃, 0.11mM, 11mL) and trisodium citrate (Na₃CA, 2.05mM, 11mL) are prepared under magnetic stirring. Then the solution of sodium borohydride (NaBH₄) is added rapidly into the solution. The stirring is kept for about 10min and then the solution is aged at room temperature overnight. This is the seed solution. In the second step, 100mL DI water is mixed with AgNO₃ (5mM, 2.5mL) and PVP (Mw=29, 000, 0.7mM, 7.5mL), Na₃CA (30mM, 7.5mL) and 0.2mL of the previous seed solution. Then the solution
is rapidly combined with L-ascorbic acid (AA, 1mM, 62.5mL) under rigorous stirring. The color slowly changes from yellow to cyan. Then the solution is cleaned by centrifugation to remove the excessive polymer and concentrated for future use. In this process, Na$_3$CA serves as the capping agent which binds to the (111) plane of the seeds, and AA is a gentle reducing agent which can deposit the Ag ions in the solution onto the seeds, thus leading to the planar growth of the particles. The shape and size of the plates are characterized by HRTEM and shown in Figure 3-13. In order to obtain the thickness of the plates, the droplet is dried down onto the grid so that the plates can stand vertically.

Figure 3-13: Characterization of silver nanoplates synthesized by seed-mediated growth. (a) High-concentrated silver nanoplates (b) Silver nanoplates dried down on the TEM grid

In Figure 3-14, the absorbance of the as-prepared solution is measured by UV-Vis spectroscopy. Since the resonance is around 750nm in the water, I do not need to grow the plates any further. If larger plates are needed, the solution prepared in the second step can serve as seeds in the next round growth. The precursor AgNO$_3$, capping agent Na$_3$CA and reducing agent AA should be added in the same way in each round.

Although there is still a small amount of spherical particles as is indicated by the small 400nm peak in the UV-Vis spectrum [85], the size distribution of the nanoplates is improved compared with the previous methods. Therefore, the Ag nanoplates synthesized by seed-mediated growth is used as antennas to transmit and extract light from MoS$_2$.  

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3.2 High-order plasmon modes in silver triangular platelet by Electron Energy-Loss Spectroscopy (EELS)

3.2.1 STEM-EELS acquisition and EELS maps

As is illustrated in Figure 3-15, EELS is performed in a Scanning Transmission Electron Microscope (STEM), in which the beam is focused and scanned over the sample area to collect loss spectra. The main advantage of the electron microscope is the nanometer spatial resolution, allowing for the near field mapping of plasmonic nanostructures. STEM-EELS is a useful technique to obtain the high-resolution mapping of plasmonic modes, as well as probe the photonic local density of states [89]. In this section, I will discuss about the working principle of EELS, and its application in probing the plasmonic modes. Moreover, I will present the experimental results from our collaborator Dr. Ritesh Sachan in Oak Ridge Laboratory.

The elastically scattered electrons only change their momentum, while the inelas-
tically scattered electrons will transfer energy to the sample. The former are collected by dark field detectors, i.e. High-Angle Annular Dark-Field (HAADF) detectors, from which the Z-contrast images can be acquired. The latter will either excite the core or valence electrons, as well as collective modes (LSP and SPPs), depending on the energy of interest. The core-loss region has energy loss higher than 50eV, and the loss-loss region has energy loss lower than 50eV. The zero loss peak (ZLP) corresponds to an energy loss of 0eV. Since typical plasmon energy is of the order of several electron volts, the FWHM of ZLP is an important factor in determining the resolution of the energy.

In terms of data acquisition, the focused electron beam scans over the sample and stops for a defined time at each position. In normal imaging mode, elastically scattered electrons are collected by HAADF detector. Electrons that do not change their trajectory are dispersed in the energy-filter and the dispersive plane is projected onto the CCD camera. The camera records the spectrum for each position sampled by the electron beam. The resultant data is a three-dimensional data cube, including two spatial coordinates and one energy loss spectrum. Figure 3-16 gives a clear illustration of the data acquisition process.
This data cube allows for the extraction of energy loss spectrum at a certain position, as well as the EELS map of a certain energy loss.

### 3.2.2 EELS mapping of plasmon modes in individual triangular antenna

As is mentioned before, plasmon resonance enables the concentration of light into sub-diffraction limited volumes. EELS has the potential to generate a full mode spectrum of plasmonic nanostructures, including bright modes and dark modes. Dark modes are present in coupled-antenna structure [68]. Their decay channel is via absorption instead of radiative damping, resulting in the quenching of nearby emitters. It is thus important to study the spectral location of such plasmon modes. In this section, I will show the experimental results from our collaborator Dr. Ritesh Sachan in Figure 3-17. The triangular plates are synthesized by the polyol process mentioned above.
Figure 3-17: EELS maps of plasmon modes in single triangular antenna (credit: Dr. Ritesh Sachan)
The intensities are proportional to the $z$-projected local photonic density of states. Multiple-order plasmon modes are discernible for all particles. The rightmost column of the images shows the bulk plasmon mode, which is 3.65eV. This mode slightly redshifts compared with the typical Ag bulk plasmon resonance, which is 3.8eV. This may arise from the presence of the substrate, i.e. TEM grid, which increases the effective permittivity of the surrounding environment. Higher order mode has larger resonance energy. Also, it can be seen that for the same order of plasmon mode, the resonance energy is smaller in antenna with larger edge length. I will discuss this in details in the next section in accompany with the FDTD simulation results.

3.3 Finite-difference time-domain (FDTD) simulation of high-order plasmon modes in triangular antennas

As is discussed in the previous sections, noble metal particles can support LSPR, and the optical excitation of higher-order harmonics, i.e. multipolar plasmon resonances, becomes possible. Such high-order plasmon modes have resonance frequency in the visible and near-infrared regions.

In this section I will demonstrate the spatial distribution of the high-order resonance calculated by FDTD. In order to calculate the plasmon eigenmodes, a circularly polarized excitation is used and the field profile monitor is placed 5nm above the structure. The light source contains two orthogonal plane waves with a 90 phase difference. Total-field scattered-field (TFSF) source is used in order to calculate the absorption, scattering and extinction cross section based on the recorded total and scattered power.

Here the edge length of the equilateral triangles are 200nm, 400nm and 600nm respectively, and their thickness is 40nm. They have round tips with radius 10nm to mimic the practical case. The calculated resonance curves, and the eigenmodes corresponding to the peaks are shown in the Figure 3-19, 3-20, 3-21, 3-22, 3-23 and
For 200nm triangular antenna, the dipole mode resonance is at 697nm and the quadrupole mode resonance is at around 410nm, which can be visualized by the z-component of the electrical field.

For 400nm triangular antenna, the dipole mode resonance is at 1100nm, the quadrupole mode resonance is at 550nm, and the octupole mode resonance is at around 458nm.

For 600nm triangular antenna, there are more eigenmodes due to larger edge length. Four of them are shown in the figure, and their resonances are 1505nm, 730nm, 596nm and 490nm.

The resonant behavior of the triangular platelet antenna arises from the interference of excited, reflected and transmitted wedge plasmons. In analogy to light propagation, the collective oscillation of the electrons is like standing wave, and the wave vector varies for different eigenmodes. Once we get the wave vectors and the corresponding energy, we can plot the dispersion curve of this kind of plasmon modes [70]. It is obvious that the resonance depends on the size, shape and material of the plate. For larger plate, there can be multiple field maxima along the edge, as long as the resonance frequency is smaller than that of the bulk plasmon mode.

Here the optical excitation only shows qualitative agreement with the EELS data. If the particular triangular plate is excited by the circularly polarized light, only
Figure 3-19: Optical resonance of triangular antenna with edge length 200nm and height 40nm

certain modes can be excited [91]. Quantitative analysis can be realized by using an array of dipoles to mimic the case of electron excitation [76], which can excite all the modes in the plasmonic structure. This is not my focus and will not be discussed in details in this thesis.
Figure 3-20: Plasmon eigenmodes of 200nm triangular antenna: dipole mode (697nm) and quadrupole mode (410nm) (upper: total field; lower: z-component of the field)
Figure 3-21: Optical resonance of triangular antenna with edge length 400nm and height 40nm

Figure 3-22: Plasmon eigenmodes of 400nm triangular antenna: 1100nm, 550nm and 458nm (upper: total field; lower: z-component of the field)
Figure 3-23: Optical resonance of triangular antenna with edge length 600nm and height 40nm
Figure 3-24: Plasmon eigenmodes of 600nm triangular antenna: 1505nm, 730nm, 596nm and 490nm (upper: total field; lower: z-component of the field)
Chapter 4

Tuning the emission of MoS$_2$ by platelet antennas

4.1 Antenna-emitter coupled system for tunable photoluminescence

In photonics, spontaneous emission arises from dipole oscillations in the exited state of atoms, molecules or quantum dots. When an optical antenna nearby acts as a local probe, the emission from a single molecule can either couple to the far field via the antenna or quench through ohmic loss. Compared with high-quantum-yield emitters, the brightness enhancement for low-quantum-yield emitters is much higher, because their intrinsic quantum yield has a larger potential to be enhanced by the antenna [39].

In this section, I will first prove this rule by calculating the fluorescence enhancement based on a simple system, i.e. a single horizontal dipole placed right below a spherical silver antenna. Then I will use FDTD to numerically calculate the photoluminescence enhancement of MoS$_2$ induced by a disc antenna.
4.1.1 Horizontal dipole coupled with spherical antenna

This section mainly deals with the analytical results adapted from reference [92, 93], to address the PL tunability of the nearby emitter with different intrinsic quantum yield. The fluorescence enhancement factor can be expressed as the product of excitation rate enhancement and quantum yield enhancement [94]. Therefore, the tunability of emission can be achieved by controlling both excitation and emission processes.

\[ f_F = \frac{\gamma_{\text{exc}} q}{\gamma_{\text{exc}}^0 q^0} \]  

(4.1)

The total decay rate of the excited dipole in the absence of antenna is the sum of radiative decay and nonradiative decay. They are both intrinsic properties of the molecule. The intrinsic quantum yield is defined as

\[ q^0 = \frac{\gamma_r^0}{\gamma_r^0 + \gamma_{nr}^0} \]  

(4.2)

This definition is based on the so-called differential quantum yield [95]. When the antenna is present, it will induce additional decay channel \( \gamma_{\text{abs}} \) due to ohmic loss. This can result in the total spontaneous decay rate enhancement \( \gamma_{sp}/\gamma_{sp}^0 \), which is called Purcell factor [40, 96, 97, 98]. The quantum yield is this case becomes

\[ q = \frac{\gamma_r}{\gamma_r + \gamma_{nr} + \gamma_{\text{abs}}} = \frac{\gamma_r}{\gamma_r + \gamma_{\text{abs}}} + \frac{\gamma_{\text{abs}}}{q^0} \]  

(4.3)

The decay rate enhancement can be represented by the energy dissipation rate enhancement, i.e. \( \frac{\gamma_{\text{abs}}}{\gamma_r} = \frac{P_{\text{abs}}}{P_0} \) and \( \frac{\gamma_r}{\gamma_r} = \frac{P_r}{P_0} \). This relationship will be discussed using classical harmonic oscillator in the next subsection.

The curvature of the antenna can be neglected when the distance between dipole and antenna is sufficiently small. Then the nonradiative decay rate enhancement can be calculated using electrostatic image theory

\[ \frac{\gamma_{\text{abs}}}{\gamma_r^0} = \frac{3}{16} \frac{1}{m} \frac{\varepsilon(\omega_2) - 1}{\varepsilon(\omega_2) + 1} \frac{k^3 z^3}{|p|^2} \]  

(4.4)

where \( z \) is the dipole-antenna distance, \( p \) is the dipole moment and \( \omega_2 \) is the dipole...
Because the scattered power $P_r$ from a particle much smaller than wavelength mainly arises from the particle's induced dipole, the induced dipole can be expressed as

$$p_{\text{induced}} = k_0^2 \frac{1}{\varepsilon_0} \vec{\alpha}_p(\omega_2) \vec{G}(r_p, r_0; \omega_2) \vec{p}$$  \hspace{1cm} (4.5)

$\vec{G}$ denotes the dyadic Green's function in free space

$$\vec{G}(r, r_0) = \frac{1}{k^2} \nabla \nabla G(r, r_0), G(r, r_0) = \frac{\exp(ik|r-r_0|)}{4\pi|r-r_0|}$$  \hspace{1cm} (4.6)

The radiative decay rate enhancement is

$$\frac{\gamma_r}{\gamma_p^0} = \frac{|p + p_{\text{induced}}|^2}{|p|^2} = |n_p + k_0^2 \frac{1}{\varepsilon_0} \vec{\alpha}_p(\omega_2) \vec{G}(r_p, r_0; \omega_2) n_p|^2$$  \hspace{1cm} (4.7)

The quasi-static polarizability of a spherical particle is

$$\vec{\alpha}(\omega_2) = 4\pi \varepsilon_0 a^3 \frac{\varepsilon(\omega_2) - 1}{\varepsilon(\omega_2) + 2}$$  \hspace{1cm} (4.8)

and the resultant radiative decay rate enhancement is

$$\frac{\gamma_r}{\gamma_p^0} = |1 + 2 \frac{a^3}{(a+z)^3} \frac{\varepsilon(\omega_2) - 1}{\varepsilon(\omega_2) + 2}|^2$$  \hspace{1cm} (4.9)

For a horizontal dipole, $p_z = 0$, the nonradiative rate enhancement becomes

$$\frac{\gamma_{\text{abs}}}{\gamma_p^0} = \frac{3}{16} Im \frac{\varepsilon(\omega_2) - 1}{\varepsilon(\omega_2)} + \frac{1}{1 + \frac{k_0^2}{2}}$$  \hspace{1cm} (4.10)

On the other hand, the excitation rate $\gamma_{\text{exc}}$ is determined by both the incident laser field $E_0$ and the secondary field induced by the antenna $E_s$. In terms of weak excitation, $\gamma_{\text{exc}} \propto |p \cdot [E_0 + E_s]|^2$. The dipole's local excitation field can be expressed in terms of free-space Green's function

$$E = E_0 + k_0^2 \frac{1}{\varepsilon_0} \vec{G}(r_0, r_p; \omega_1) \vec{\alpha}(\omega_1) E_0$$  \hspace{1cm} (4.11)
The excitation rate enhancement is

\[
\frac{\gamma_{\text{exc}}}{\gamma_{\text{exc}}^0} = \left| \frac{n_p \cdot \left[ \mathbf{I} + k_0^2 \frac{1}{\varepsilon_0} \mathbf{G} \left( r_o, r_p; \omega_1 \right) \alpha \left( \omega_1 \right) n_{E_0} \right]}{|n_p \cdot n_{E_0}|^2} \right|^2
\]

Substitute the polarizability of spherical particle into the above equation, the excitation rate enhancement becomes

\[
\frac{\gamma_{\text{exc}}}{\gamma_{\text{exc}}^0} = 1 + 2 \frac{a^3}{(a+z)^3} \frac{\varepsilon(\omega_1) - 1}{\varepsilon(\omega_1) + 2}
\]

Here \( \omega_1 \) and \( \omega_2 \) are excitation and emission frequencies, respectively. In order to compare this case with the case of MoS\(_2\), I assume the radius of the silver spherical antenna is \( a = 40\text{nm} \), and the emission wavelength of the dipole is 670nm. The permittivity of silver is \( \varepsilon = -16.561 + 1.3247i \), according to Palik data and ignoring the dispersion [99].

The quantum yield enhancement curve in Figure 4-1 shows that the enhancement factor is much larger for low-quantum-yield emitters. The quantum yield increases monotonously for \( q^0 = 1 \) emitter.

![Figure 4-1: Quantum yield enhancement for emitters with different intrinsic quantum yields](image)

Therefore, the total emission enhancement is also much larger for low-quantum-
yield emitters. In particular, for $q^0 = 1$ emitter in Figure 4-3, the enhancement is largest when the dipole-antenna distance is around 10nm. Furthermore, when the distance is smaller than 4nm, the enhancement factor is less than 1, which indicates the emission quenching due to the dominant of ohmic losses.

![Figure 4-2: Emission enhancement. (a) Emitters with different intrinsic quantum yields (b) Emitter with $q^0 = 1$](image)

This simple analytical model containing horizontal dipole and spherical antenna provides qualitative illustration on how the emission enhancement will change with respect to the dipole-antenna distance, and when the emission quenching or enhancement will happen.

### 4.1.2 Model MoS$_2$ coupled with disc antenna

The analysis in the previous section proves that the enhancement or quenching of PL intensity can be controlled by varying the dipole-antenna distance. Besides, the emitters with lower intrinsic quantum yield has larger potential to be enhanced by the nearby antenna.

Here I use the disc antennas which are synthesized by seed-mediated growth, because they have relatively narrow size distribution as is shown in Chapter 3. In addition, there is an overlap between the scattering spectrum of a single disc and the photoluminescence spectrum of MoS$_2$. 
In the model, I assume there is no coupling between antennas. Besides, experiments have demonstrated that the emission orientation of monolayer MoS$_2$ is in-plane [$100$]. So MoS$_2$ flake can be represented as in-plane dipole. But since the disc antenna has finite size while the dipole is just a point source, both the excitation rate and quantum yield enhancement should be averaged over different locations under the antenna.

The excitation rate enhancement is represented as

\[
\frac{\gamma_{exc}}{\gamma_{exc}^0} = \frac{|E_{exc} \cdot n_p|^2}{|E_{exc}^0 \cdot n_p|^2}
\]  

Because MoS$_2$ is excited by 532nm laser in the experiment, 532nm plane wave is used as light source in the simulation. From the expression of the field enhancement, we know that z-component of the field will not excite in-plane dipole, so we only need to consider x-component and y-component of the field. Here assume the dipole is oriented in x direction for simplicity. The field enhancement is sampled at different locations under the antenna. In FDTD simulation, the antenna is placed at a certain distance above the SiO$_2$/Si substrate. The field profile is sampled by a 8 by 8 grid,

Figure 4-3: Scattering of a single disc in the air (diameter=80nm, thickness=6nm) and the photoluminescence of MoS$_2$.
and the dimension of each square is 10nm by 10nm, just cover the region under the antenna. The field intensity \( (E_2^2) \) at the center of each square is recorded and averaged by Matlab code. Since 532nm incidence does not match the resonance frequency of the antenna, we can anticipate that the enhancement is not so high.

(a) \( |E / E_0| \)

(b) \( |E / E_0| \)

Figure 4-4: Simulated field enhancement. (a) Representative field enhancement when gap=6nm (b) FDTD simulation setup

The quantum yield enhancement is calculated by connecting it with the energy dissipation rate. This has been proved in details in Novotny’s book [94]. Here I will use a classical model to capture the main idea and illustrate their relationship.

In terms of dipole radiation, the radiated power into far field can be determined by integrating the Poynting vector over a closed spherical surface. The average radiated power is

\[
P_0 = \frac{|p|^2}{4\pi\varepsilon_0\varepsilon} \frac{n^3\omega_4}{3c^3} \quad (4.15)
\]

The rate of energy dissipation is given by

\[
P = \frac{dW}{dt} = \frac{\omega}{2} Im[p^* \cdot E(r_0)] \quad (4.16)
\]

where \( E \) is the sum of the dipole field \( E_0 \) and the scattered field \( E_s \): \( E(r_0) = E_0(r_0) + E_s(r_0) \). Since \( P_0 \) represents the radiated power in homogeneous environment
\[ P_0 = \frac{\omega}{2} Im[p^* \cdot E_0(r_0)] \]  

(4.17)

The normalized rate of energy dissipation can be obtained

\[
\frac{P}{P_0} = 1 + \frac{6\pi \varepsilon_0 \varepsilon}{|p|^2} \frac{1}{k^3} Im[p^* \cdot E_s(r_0)]
\]

(4.18)

which depends on the secondary field at the dipole after it has been scattered in the environment.

The classical picture of spontaneous decay can be described by considering an harmonically oscillating dipole whose intrinsic frequency is at its emission frequency. As the dipole oscillates, it will radiate energy and the dipole moment will decrease. The decay time corresponds to the time when the dipole's energy decreases to \(\frac{1}{e}\) of its original value.

\[ \omega_n = \sqrt{\frac{k}{m}} \]

Figure 4-5: Classical picture of dipole oscillation

In the homogeneous environment, i.e. in the absence of antenna, the equation of motion for the oscillating dipole is

\[
\frac{d^2}{dt^2} p(t) + \gamma_0 \frac{d}{dt} p(t) + \omega_0^2 p(t) = 0
\]

(4.19)

where \(\gamma_0\) is the damping constant.

The solution for dipole moment is

\[ p(t) = Re[p_0 e^{-i \omega \sqrt{1 - (\gamma_0^2 / 4 \omega_0^2) i} e^{-\gamma_0 t / 2}}] \]

(4.20)

The damping rate not only attenuates the dipole moment but also shifts the resonance frequency. Assume the damping rate is much smaller than the oscillation
frequency, i.e. $\gamma_0 \ll \omega_0$, the average energy is the sum of the kinetic and potential energy

$$W(t) = \frac{m}{2q^2} [\omega_0^2 \dot{p}(t)^2 + \dot{\omega}(t)^2] = \frac{m\omega_0^2}{2q^2} |p_0|^2 e^{-\gamma_0 t}$$  \hspace{1cm} (4.21)

Then the lifetime is $\tau_0 = 1/\gamma_0$.

When connecting the energy dissipation with the power of dipole oscillation, we should introduce the intrinsic quantum yield $q^0$, which denotes the fraction of energy transformed to radiation, so we have

$$W(t=0) - W(t) = q^0 \int_0^t P_0(t')dt'$$  \hspace{1cm} (4.22)

The decay rate in the homogeneous environment can thus be expressed as

$$\gamma_0 = q^0 \frac{1}{4\pi\varepsilon_0} \frac{2q^2\omega_0^2}{3mc^3}$$  \hspace{1cm} (4.23)

In an inhomogeneous environment, i.e. in the presence of antenna, the dipole will experience a driving field that arrives back to the dipole after it has been scattered in the environment. In this case, the equation of motion is

$$\frac{d^2}{dt^2} p(t) + \gamma_0 \frac{d}{dt} p(t) + \omega_0^2 p(t) = \frac{q^2}{m} E_s(t)$$  \hspace{1cm} (4.24)

Here the secondary field is similar to the one discussed in the derivation of radiated power. Considering the form of dipole moment in the homogeneous environment case, we can use the following trial solutions for this differential equation

$$p(t) = Re[p_0 e^{-i\omega t} e^{-\gamma_0 t/2}]$$  \hspace{1cm} (4.25)

$$E_s(t) = Re[E_s e^{-i\omega t} e^{-\gamma_0 t/2}]$$  \hspace{1cm} (4.26)

Comparing the imaginary part of the left hand and right hand side, plugging in the expression for $\gamma_0$, and set $q^0 = 1$, we have

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Thus, we can get the connection between normalized decay rate and normalized radiated power

$$\frac{\gamma}{\gamma_0} = 1 + \frac{6\pi\varepsilon_0\varepsilon}{|p|^2} Im[p^* \cdot E_0(r)]$$

(4.27)

This is the essential relationship used in calculating quantum yield enhancement by FDTD simulation.

The quantum yield enhancement is

$$f_Q = \frac{q}{q^0} = \frac{\frac{\gamma}{\gamma_0}}{\frac{\gamma}{\gamma_0} + \frac{2\alpha_{nh}}{\gamma_0} q^0 + (1 - q^0)} = \frac{f_r}{(f_r + f_{nr})q^0 + (1 - q^0)}$$

(4.29)

where the radiative decay rate enhancement is $f_r = \frac{\gamma}{\gamma_0}$, and the nonradiative decay rate enhancement is $f_{nr} = \frac{2\alpha_{nh}}{\gamma_0}$. They are independent of the intrinsic nonradiative decay channel inside the emitter, so they can be obtained by using a dipole source with $q^0 = 1$ in FDTD. A representative simulation setup with the dipole source placed at a certain position is shown in Figure 4-6.

![Figure 4-6: Representative FDTD simulation for quantum yield enhancement](image)

In a typical simulation, one small box around the dipole source is used to record the total power, while another box enclosing the dipole and antenna is used to record...
the radiation power into free space. The nonradiative power is thus the difference between these two recorded power. In addition, the radiative power in the absence of antenna is also recorded, by the same box. All the power recorded correspond to dipole emission at 670nm. Since the parameter we care about is the optimal distance between the dipole and the antenna, the small box should be small enough and not touch the antenna. The mesh size is 2nm, so the gap is multiple times mesh size. Since the dimension of small box is 4nm, when the gap is smaller than 4nm the calculation does not make sense, and the quantum effect should be taken into account. Therefore, I change the gap from 6nm to 20nm in the simulation. Furthermore, the enhancement factor is calculated by scanning the dipole in the different locations under the antenna and taking the average value, similar as before.

After obtaining the average radiative and nonradiative decay rate, the quantum yield can be calculated based on these two values. I plot the quantum yield enhancement for emitters with different quantum yield to emphasize the effect of antenna on low-quantum-yield emitter, such as MoS$_2$. Here I assume that different emitters have the same emission frequency.

It can been seen that the antenna can result in both radiative and nonradiative rate enhancement. When the gap is smaller than 8nm, the nonradiative decay channel is dominant. Then both radiative and nonradiative rate enhancement decrease as the gap increases. The maximum quantum yield enhancement happens at gap 8nm. This trend shows qualitative agreement with the analytical result in the previous section.

Taking the product of the field enhancement and quantum yield enhancement, we can get the total average emission enhancement $\bar{f}_F = \bar{f}_E \bar{f}_Q$. The enhancement can be up to 18 times, and then drop rapidly when the gap increases.

The limitation of this model is that we cannot get the enhancement factor when the gap is sufficiently small. So we do not know where the emission quenching will happen. Here the simulation result serves as a guidance to the experiment in which a spacer layer is required to tune the PL intensity of MoS$_2$.
In order to verify the effect of gap thickness on the tunability of PL, aluminum oxide was deposited on MoS$_2$ by atomic layer deposition (ALD). Precursors were trimethyl aluminum (TMA) and H$_2$O and the ambient temperature was 175°C. The thickness of Al$_2$O$_3$ was controlled by the cycles of deposition. Each cycle will deposit 1.9 Å to 2.0 Å Al$_2$O$_3$. After ALD, the thickness of the spacer layer ranges from 6nm to 20nm, which follows the simulation above.

Since the refractive index of Al$_2$O$_3$ is about 1.768 in the visible range, it will
affect both the excitation and emission of MoS$_2$. This effect can be seen by placing the dipole at a certain position under the antenna and compare the radiative and nonradiative power.

![Graph showing simulated radiative and nonradiative power with and without spacer layer.](image)

Figure 4-8: Simulated radiative and nonradiative power with and without spacer layer.

From the simulation results, we can see that when we add the spacer layer, the radiative decay will be very small compared with nonradiative decay for a dipole emitting at 670nm. The maximum decay power also shows a shift. The simulation setup was the same as the previous section, except that a Al$_2$O$_3$ was added in the gap. The simulated PL enhancement is about 5.3 times, which is smaller than the case when no spacer layer is added. This agrees with the fact that radiative power becomes very small.

The micro-PL measurements were conducted on the as-deposited samples. 10 $\mu$L droplet of platelet antenna solution was drop-cast onto the samples. Then the samples were washed with DI water and blow-dried with nitrogen gas to avoid the formation of clusters.

For each sample, three curves were collected with the laser spot probing different locations of the sample, and then baseline was subtracted from the signal. The photoluminescence enhancement can be clearly seen in Figure 4-10. The difference
Figure 4-9: Simulated photoluminescence enhancement (with Al₂O₃ as spacer layer). (a) Average field enhancement under the antenna (b) Average radiative and nonradiative decay rate enhancement (c) Average quantum yield enhancement (d) Theoretical PL enhancement
Figure 4-10: Measured photoluminescence enhancement for different \( \text{Al}_2\text{O}_3 \) thickness. (a) 6nm (b) 8nm (c) 10nm (d) 16nm (e) 18nm (f) Ratio of PL intensity (black dots: PL intensity enhancement; red dots: average PL intensity enhancement)
in the maximum PL intensity from the same sample arises from the variation of plate distribution on MoS$_2$. The irregular sharp peaks in Figure 4-10(c) is due to the occasional presence of particle clusters. The average ratio of PL intensity was denoted by red dots. In general, the ratio of PL intensity shows qualitative agreement in both trend and magnitude with the simulated results, except that the sample with 12nm spacer layer deviates from the trend. The maximum enhancement can be more than 2 times.

The discrepancy between experiments and simulation may arise from many factors. First, the coverage of the antennas on MoS$_2$ must be smaller than the scenario in the simulation, in which I only consider the local field right below the antenna. Second, the collection efficiency $\eta$, which denotes the probability of the photons reaching the detector, should be included in the PL enhancement factor. This is related to the radiation pattern of the dipole-antenna system, NA of the microscope and the sensitivity of the CCD camera etc. Furthermore, in the simulation model I have treated MoS$_2$ as a horizontal dipole and ignored its optical properties, but actually it has high refractive index around $n = 6 + 2i$ [101] which will shift the resonance of the antenna. Despite of the low enhancement, these single crystalline platelet antennas still hold promise in improving the photoluminescence of monolayer MoS$_2$, which is a low-quantum-yield emitter.

Another advantage is that the feature of B exciton is still discernible. This is illustrated in Figure 4-12 where A and B excitons are fitted with Lorentz model. This feature is important because the spin-orbital splitting leads to many promising applications, as is summarized in Chapter 1.

Furthermore, according to the analytical results in the previous section, PL quenching is expected to happen when the gap between the antenna and the emitter is sufficiently small. However, PL enhancement is still present in Figure 4-13 when the antennas are in direct contact with monolayer MoS$_2$. 

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Figure 4-11: A and B exciton peaks fitting using Lorentz model $y = y_0 + \frac{2A}{\pi} \frac{1}{(x-x_o)^2 + \frac{w^2}{4}}$ (dash line) before (solid black line) and after (solid red line) PL enhancement.

Figure 4-12: PL curves when the platelet antennas are in direct contact with monolayer MoS$_2$. 
4.2 Time-resolved spectroscopy and preliminary experimental results

4.2.1 Time-resolved spectroscopy

The dynamic properties of materials on a femtosecond timescale can help us determine their decay rate. Pump-probe spectroscopic techniques are important ultrafast optical tools for us to understand the dynamic electronic or optical properties. In such technique, a high-intensity pump pulse perturbs the sample from equilibrium, then a weak probe pulse measures the change in transmission and reflection at a certain time delay [102]. The time delay depends on the pump and probe path length, which can be controlled by the delay stage. Sampling technique is used to reconstruct the time-resolved photoluminescence. One of the critical parameters is the minimum time resolution, which is limited by the pump and probe durations and the interval between the time delays.

Figure 4-14 shows a representative degenerate pump-probe setup. The pump and probe wavelength are the same, and they are separated by polarization optics. The material properties, i.e. differential transmission or reflection, are sampled by the weak probe pulse which should not significantly change the material properties. If we use lock-in detection, the change can be reflected in the voltage. The pump beam is chopped at frequency $f_e$, while the probe beam is not chopped. If we use a 50% duty cycle, half of the probe beam will be incident on the sample without the perturbing of the pump beam.

The differential transmission or reflection is related to the change in the absorption, which depends on the joint density of states of the material [102]. So we can imagine that the pump-probe spectroscopy can be used to measure the change in electron occupation states. In order to obtain the full time-resolved dynamics, multiple measurements at different time delays are required. This technique is obviously inefficient. An alternate method of rapidly acquiring signals employs a streak camera demonstrated in Figure 4-15. The optical field coming from the sample is incident
Figure 4-13: Working principle of pump-probe setup. (a) Degenerate pump-probe setup (b) An illustration of differential transmission and reflection at a certain time delay using lock-in detection [102]

Figure 4-14: Operating principles of a streak camera [103]
on the photocathode that can emit electrons through photoelectric effect. The electrons then pass through a time-dependent field, and then a time-to-space mapping is obtained on a phosphor screen. Therefore, axis in the perpendicular direction corresponds to temporal axis, while the axis in the horizontal direction corresponds to the wavelength of incident light.

4.2.2 Time-resolved photoluminescence of monolayer MoS$_2$

The reported decay time of MoS$_2$ is around 100ps [104, 105], and it is temperature- and substrate- dependent [104, 28]. The Time-resolved PL curve of bare MoS$_2$ was measured by Dr. Dafei Jin and our collaborator in UC-Berkeley. The sample was pumped by the femtosecond laser (Inspire), and the signal was collected by the streak camera (Hamamatsu C10910-02). The measured signal was the convolution of the signal from the sample and the point spread function (PSF) of the system. After deconvolving the PSF from the detected signal, we can obtain the real time-resolved PL signal $y = 1.216e^{-0.17}$. The decay time 0.917ps is substantially smaller than the reported data. Since the nominal time resolution of the streak camera is 1ps, this result would not be valid. Figure 4-16 shows the experimental setup and the obtained data. The unexpected short decay time may arise from the substrate we use. If h-BN substrate is used or the sample is suspended, we may expect higher quantum yield and thus longer decay time [28, 22]. Thus we will not seek to measure the Purcell factor, which denotes the enhancement of the total spontaneous emission rate $\gamma_{sp}/\gamma_{sp}^0$ [40].
Figure 4-15: Time-resolved PL measurement. (a) Experimental setup (b) Measured point spread function (PSF) of the system (c) Measured data (black dots) and fitted curve (red solid line) (The red curve was obtained by setting the time-resolved signal as $y = Ae^{-\frac{t-t_0}{\tau_o}}$, and then convolved with PSF curve. The fitting parameters are A, $t_0$ and $\tau_o$.) (d) Real time-resolved PL signal
Chapter 5

Summary and outlook

5.1 Summary

In this master thesis, I have investigated the interaction between optical antenna and emitter, by studying the enhanced spontaneous emission from monolayer MoS$_2$ with single crystalline platelet antennas. This basic scheme can also be applied to many other antenna-emitter systems, such as antenna-coupled quantum well and quantum dot, to develop more efficient emitters. For monolayer MoS$_2$, which is both a promising two-dimensional semiconductor and a low-quantum-yield emitter, some researchers have reported the enhanced emission from MoS$_2$ with lithographically defined plasmonic nanoantennas [106, 107] and plasmonic nanocavity [108] during the time of my work. Here I demonstrate a more economic and promising way in tuning the emission of MoS$_2$ by colloidal platelet antennas.

My work can be summarized as follows:

First, I seek to colloidally synthesize single crystalline silver platelet antennas for high-quality near-field imaging. The antennas of this particular shape have tunable resonance ranging from 350nm to 1000nm, covering the whole visible spectrum. The main methods that can be used to obtain polygonal plates are polyol process, light-mediated growth and seed-mediated growth [49]. With polyol process, I can obtain platelet antennas with well-defined polygonal shapes, and the yield has been improved with high-power white light illumination. These plates have already satisfied the re-
quirements of near-field imaging by CL and EELS. Although light-mediated growth seems to be a promising way to obtain platelet antennas with narrow size distribution, all the documented methods use high-power LED and laser. Albeit with wide size distribution, these plates grown by polyol process can serve as broadband absorbers. Then I turn to seed-mediated growth to get platelet antennas with narrow size distribution and resonance close to the emission line of MoS$_2$. The plates synthesized in the first-round growth have resonance around 750nm in the water. The as-prepared platelet antennas have thickness below 10nm. Furthermore, I have qualitatively compared the high-order plasmon modes in triangular plates with the EELS data from our collaborator. Since the incident source is circularly polarized light and the plate has 3-fold symmetry, only certain resonant modes can be excited [91].

Second, I have investigated the thickness-dependent properties of MoS$_2$. The samples are prepared by micro-exfoliation onto a SiO$_2$/Si substrate to enhance the optical contrast. Besides the contrast, both micro-PL and Raman spectra can offer abundant information on the layer-dependent optical properties of MoS$_2$. The crossover from indirect bandgap in bulk MoS$_2$ to direct bandgap in monolayer MoS$_2$ leads to the absence of indirect transition in the PL curve. In addition, the decreasing restoring force results in the softening of the out-of-plane phonon mode in the Raman spectra. In order to widen the application of MoS$_2$, I have also tried to transfer the flakes onto gold substrate by spin coating PMMA as a sacrificial layer.

Third, I have been looking for a feasible way to study the photoluminescence enhancement in this antenna-emitter coupled system. It is well known that both the decay rate and PL intensity of the emitters can be enhanced by the nearby lossy medium, such as metallic structure and photonic crystal, which can increase the local photonic density of states. Both the total spontaneous emission rate enhancement, i.e. Purcell factor, and the PL intensity enhancement arise from the enhancement of radiative and nonradiative decay. The nonradiative decay can come from various decay channels, which may be induced by plasmonic nanocavity, nanowire, grating, antenna, etc. In my case, the only nonradiative decay channel is due to the ohmic loss in the silver platelet antenna. Initially, I seek to measure the time-resolved
PL of MoS$_2$ and the corresponding Purcell factor, but the short decay time, which agrees with its low quantum yield, hinders the further investigation of decay rate analysis. Then I turn to study the enhanced photoluminescence in a simple system containing a horizontal dipole and a spherical antenna. The analytical results provide two important pieces of information: first, the PL of low-quantum-yield emitter has larger potential to be enhanced by the antenna; second, photoluminescence quenching and enhancement is governed by the dipole-antenna distance. Next I have studied the tunable emission in my system by both experiments and FDTD simulation. The numerical simulation is conducted by simulating both the excitation and emission processes. Here I treat MoS$_2$ as an in-plane dipole in line with the experimental observation reported by the literature, and scan the dipole at different locations under the antenna to take account of the geometry effect. The presence of the spacer layer shifts the plasmon resonance and thus changes the PL enhancement. The PL enhancement in the experiments is a bit smaller than the simulated results. This may arise from the simulation model and the so-called collection efficiency of the PL setup. In general, the PL enhancement versus spacer layer thickness qualitatively agrees with the trend and magnitude in the simulation. One limitation of the numerical model is that it cannot tell when PL quenching will happen because there should be a finite distance between the antenna and the box recording the total power. In the experiments, I have not observed the quenching effect when the antennas of same concentration are in direct contact with MoS$_2$.

5.2 Outlook

In general, I have demonstrated an economic and promising strategy to tune the spontaneous emission of the emerging two-dimensional semiconductor MoS$_2$. The maximum PL enhancement can be more than 2 times. Besides, both A and B exciton peaks are discernible after enhancement. Since the spin-orbital splitting and the resulting A and B excitons carry abundant information, it can facilitate the advancement of valley-based optoelectronic applications of MoS$_2$ [28, 33]. With the platelet
antennas, there is no need to transfer MoS$_2$ onto other substrates, such as photonic crystal [109] and hBN [28], to improve the quantum yield. Moreover, the ultrathin platelet antenna together with monolayer MoS$_2$ hold promise for the development of on-chip emitters.
Bibliography


