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TWO DIMENSIONAL MATERIALS:

NEW OPPORTUNITIES IN PHOTONICS

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ABSTRACT

Silicon and silica optical systems have become the primary materials of choice for visible and near-infrared optical devices. However, these materials inherently lack a direct band gap and their crystal symmetry limits second-order optical nonlinearity. In order to make next-generation system-on-a-chip devices, other materials must be incorporated into the system to integrate these properties into the system. To minimize propagating wave perturbations in the pre-existing system, these materials should be made as small as possible, fundamentally limiting light-matter interaction. However, new classes of two-dimensional materials that have been recently been discovered possessing both excellent optical properties, such as extraordinary nonlinear susceptibility, and an atomic thickness, making them excellent candidate materials to integrate into optical systems lacking these properties.

This dissertation covers work done to characterize and engineer the optical properties in two-dimensional (2D) materials in an effort to integrate them in optical systems. First, a brief introduction is provided in Chapter 1. Chapter 2 discusses the extraordinary second harmonic generation (SHG) in mono- and few-layered Transition Metal Dichalcogenides (TMDs). It is discovered that monolayer TMDs have susceptibilities over three orders of magnitude larger than typical nonlinear crystals. This work is expanded in Chapter 3, where by synthesizing alloy TMD monolayers, we can tune the monolayer nonlinear susceptibility, allowing further opportunities for engineering 2D materials for optical applications.

Chapter 4 covers a method to enhance the light-matter interaction in 2D materials by utilizing a simple nanocavity substrate. Using this simple MoS$_2$/Al$_2$O$_3$/Al substrate, we can optimize the monolayer absorption and emission by tuning the oxide thickness layer, increasing the exclusive MoS$_2$ absorption. In order to further increase this light-matter interaction with 2D materials, monolayers must be integrated into higher Q cavities. To demonstrate stronger light-matter enhancement capabilities of ultra-high-Q microresonators, Chapter 5 describes a method to enhance the particle detection capabilities of microresonators using Raman spectroscopy, demonstrating particle detection and characterization capabilities that could become an excellent platform to further increase the light-matter interaction with 2D materials. Finally, Chapter 6 concludes the dissertation by looking forward to future capabilities of 2D and microresonator systems.
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Chapter 1

Introduction

Silicon and silica optical elements have been the focus of intense research and development since the 1920’s when the first silica optical fibers were demonstrated[1]. Since then, silicon and silica systems have become the fundamental materials platform for guided optical transmission of light in both glass optical fibers[2] and silicon on-chip waveguides[3]. With modern transmission speeds over 50 Gb/s[4] and with over 2 billion kilometers of optical fiber used in communication systems today, silica fibers are the dominant form of long distance communication used today[5]. Similarly, silicon-based on-chip devices have been demonstrated as an effective medium for on-chip optical devices[6, 7, 8, 9], and have already been demonstrated as the future of biological[10] and chemical sensing[11]. However, as the next generation of optical devices is being developed, there is an increasing demand for system-on-a-chip silicon systems to perform at higher throughput and still function as optical sources or detectors[12].

Fundamentally, silicon based systems are limited by their lack of a direct band-gap and second order nonlinear susceptibility[13, 14] which limits their systems to higher-order optical nonlinearities[15]. Efforts to enhance silicon and silica waveguides have led to the development of new waveguide systems adding second-order nonlinearity or absorption/emission by engineering the waveguide system[16, 17]. One promising method to do this is to add new properties to waveguides through evanescent coupling; as the field that evanescently leaks out from the waveguide interacts with new materials, it can impart optical functionalities in those materials that would otherwise be limited in silicon optics[18, 19]. In order to functionalize the waveguide and reduce system size, these coupled materials must remain thin to minimize perturbations to the propagating wave[20, 21].
This fundamentally reduces the light-matter interaction within the secondary material, reducing its impact on the system. However, newly engineered atomically thin materials, which have extraordinary optical properties and inherent atomic thickness, would make excellent candidate materials to introduce new functionalities into these optical systems. These Two-Dimensional (2D) van-der-Waals materials are those that contain an atomic plane of atoms bonded stronger to one another than to the neighboring plane[22]. This allows a single atomic sheet to be formed, often sub-nanometer in thickness. Due to the containment in a single atomic sheet, 2D materials often have different properties than when in their bulk forms, and these often change further based on the number of atomic layers contained in the sheet[23, 24, 25]. This makes mono- and few-layered atomic sheets excellent platforms for device integration into system-on-a-chip devices.

Atomically thin materials garnered high interest after Novoselov and Geim were awarded the Nobel Prize for their discovery of graphene in 2004[26]. As a single layer of carbon atoms, graphene provided a way to fabricate exceptionally thin conductors for a wide variety of electronic and optical systems[22]. Continual development in atomically thin graphene led to the discovery of many other types of atomically thin and layered materials, covering the full range of conductors (graphene)[26], insulators (hexagonal Boron-Nitride)[27], and semi-conductors (transition metal dichalcogenides[24, 28], black phosphorous[29]). Of these, transition metal dichalcogenides (TMDs) are of particular interest, as their direct band gap in monolayer form makes them excellent materials for electronic and optical applications[24].

This dissertation will cover optical characterization and device fabrication using these newly developed 2D and layered materials. First, chapter 2 covers second harmonic generation in 2D and layered TMDs, a fundamental property missing from silicon and silica waveguides[25, 30]. A review of 2D and layered TMDs are briefly covered before demonstrating that the centrosymmetric crystal structure of layered TMDs can generate or suppress second harmonic signals by varying the number of layers in the material. In order to characterize the second order nonlinear susceptibility, a model is
formed using the 2D layer as a nonlinear sheet source before obtaining the second order nonlinear susceptibility of monolayer TMDs in the order of nm/V, several orders of magnitude larger than common nonlinear crystals[31]. Theoretical density functional theory calculations are used to calculate the theoretical value of monolayer WS$_2$’s second order nonlinear susceptibility, demonstrating good order of magnitude agreement with the measured value. Finally, two applications of SHG on 2D materials are brought forth: first, by using polarized SHG detection, one can probe the crystal symmetry and orientation of the 2D material, useful when growing large sheets of 2D materials; and finally, 2D WS$_2$ is used to perform collinear frequency resolved optical gating to demonstrate the material as an excellent platform for optical pulse characterization[32].

Due to new methods to easily vary the dopant concentrations of 2D TMD monolayers, new alloy heterostructures have been synthesized with tuneable band gaps and Raman peaks[33]. In chapter 3, we expand upon the second order nonlinear susceptibility work in chapter 2 by demonstrating that the nonlinear susceptibility can be engineered by varying the doping in the TMD alloy. Sum-Frequency Generation (SFG) is used to probe the nonlinear spectrum of 2D materials, demonstrating a method to characterize the nonlinear susceptibility spectrum. By comparing pure WS$_2$ and MoS$_2$ to an engineered W$_x$Mo$_{1-x}$S$_2$ alloy, we demonstrate that the nonlinear SFG signal can be modified by changing the composition of the material. Therefore, we demonstrate that the nonlinear susceptibility of 2D monolayers can be tuned by varying the concentration of the doping in the alloy layer. This is important for many nonlinear processes, such as complex laser pulse analysis, where an uneven nonlinear spectrum can lead to problems in pulse retrieval [32].

Although the atomically thin properties of layered TMDs are utilized in chapters 2 and 3 to achieve extraordinary nonlinear generation, the light-matter interaction of the 2D materials is weak due to their inherent atomic thickness. Ultimately, this leads to low absorption and emission from the material simply because there are few atoms to absorb and emit photons. In order to improve the light-interaction, chapter 4 proposes a simple solution by implementing an optical MoS$_2$/Al$_2$O$_3$/Al
nanocavity substrate[34]. By varying the oxide thickness in this cavity, one can tailor the absorption of the cavity, increasing the exclusive absorption in 2D MoS$_2$ to over 70% (for $\lambda = 450$nm). Photoluminescence (PL) is probed as an indication of the enhanced light-matter interaction, and experimentally measured PL generation is compared across substrates with various oxide thicknesses. Further calculations are performed to demonstrate that the nanocavity structure also modifies the optical emission of the MoS$_2$ in the cavity, leading to increased opportunities to engineer optical devices with 2D materials. This system is an effective replacement for conventional SiO$_2$/Si contrast-enhancement substrates, and would provide a platform to improve the performance of optical detectors and emitters based on 2D materials.

Using the nanocavity substrate engineering in chapter 4, we demonstrate that we can significantly enhance the light-matter interaction using optical resonators. However, the nanocavity is limited by the fundamental Q factor of the cavity. In order to significantly enhance the light-matter interaction for 2D materials, a higher Q cavity must be implemented. To this end, we would like to study the materials in the setting of ultra-high-Q microresonators[35]. These devices have been utilized as sensors for viruses and nanoparticles[36, 37], and are the next generation platform for enhanced light-matter interaction[38]. To demonstrate the capabilities of microresonator devices for micro-material systems, chapter 5 describes a method we have developed to enhance microresonator particle detection and characterization as a step towards integrating them with 2D films. Current particle detection methods using microresonators rely on perturbing the mode within the resonator though a change in refractive index, leaving them susceptible to the index of the particle. To enhance the particle characterization capabilities of this detection method, Raman spectroscopy is used to determine the type of particles adhered to the resonator[39]. By collecting the Raman scattering from the adhered particle, the material can be identified label-free, enhancing the resonator as a particle sensor. Furthermore, the resonator itself can also enhance the Raman scattering of the particle through the intense field built up within the resonator. Raman spectra are provided for resonance
enhanced Raman spectroscopy and fiber-taper based methods, demonstrating that the microresonator enhances the Raman detection capabilities.

Finally, chapter 6 concludes the dissertation by looking forward to future capabilities of 2D and resonator systems. A brief summary is provided for each chapter and ideas for future applications integrating 2D and silica fiber systems are presented.
Chapter 2

Second Harmonic Generation in Two-Dimensional Materials

Two-Dimensional and layered materials provide unique opportunities and challenges for optical devices and applications[22]. In particular, the family of Transition Metal Dichalcogenide (TMD) layered materials have garnered high interest in optical devices due to their different optical properties from their bulk forms[28, 40, 41, 42, 43]. As bulk crystals, TMD materials have an indirect bandgap and a centrosymmetric crystal structure, making them a poor choice for both active and nonlinear optical applications. However, as the layer number decreases, monolayered TMD materials transition to a direct band gap, making them excellent materials for photoluminescence generation (PL)[24, 44]. Furthermore, they also have demonstrated to be excellent nonlinear optical materials due to their extremely high nonlinear susceptibilities and unique properties varying rapidly with single layer thickness changes[25, 30, 43, 45].

Due to the varying effects of TMD materials as mono- and few-layer materials, it is important to relate the strong nonlinear susceptibility of these materials to their changing structure[25]. In this chapter, we study mono- and few-layer TMD materials Second Harmonic (SH) response. As monolayer materials, TMDs have second order nonlinear susceptibilities on the order of nm/V, three orders of magnitude larger than typical nonlinear crystals [25, 30]. However, as the number of layers in the material change, the SH response varies rapidly. With even number of layers, TMD crystals have no second harmonic generation (SHG) (D\textsubscript{3d} symmetry), and as odd number of layers, TMDs have reducing SHG as the layer number increases (D\textsubscript{3h} symmetry) [30]. This is due to the unusual crystal structure of layered TMD materials, as the bulk 2H phase of the crystal is centrosymmetric, resulting in a vanishing second order nonlinear susceptibility. However, this symmetry is broken in few odd numbered layers, creating a strong second nonlinear susceptibility. Furthermore, by
calculating the second order nonlinear susceptibility using Density Functional Theory (DFT) simulations, we discover that the large increase in nonlinear susceptibility is the result of resonance in the band structure as well as an enhanced joint density of states[25].

Finally, to conclude this chapter, we present two applications for SHG in 2D TMDs: polarized crystal symmetry probing[25, 30] and frequency resolved optical gating (FROG) pulse characterization[32]. Using polarized SHG, we demonstrate that the SHG response of the 2D material is highly dependent on the pump polarization and the crystal axis. This allows the crystal symmetry of the 2D material to be probed, demonstrating an effective method to determine crystal orientation of the material. This can be a useful tool in determining the orientation of grain boundaries of thin film TMDs[46]. Finally, we demonstrate that, due to the inherent atomic thickness of monolayer TMDs, they are excellent materials for optical laser pulse characterization. By utilizing their atomic thickness and inherently wide phase matching bandwidth, monolayer TMDs are demonstrated as a SHG medium for SHG-cFROG femtosecond laser pulse characterization.

2.1 Single- and Few- Layered Transition Metal Dichalcogenides

Transition Metal Dichalcogenide materials have recently garnered interest due to their van-der-Waals layered structure[22]. Formed by tight bonding atoms along two dimensions weakly bonded along the third dimension, TMDs have a layered structure, allowing them to be fabricated as mono- and few-layered materials. TMD materials are compounds of the MX$_2$ form, where M = W, Mo, Ti, … transition metal elements and X = S, Se, Te, … chalcogen elements. TMD materials have a hexagonal crystal structure of P6$_3$/mmc, which has varying crystal symmetry based on the number of layers in the material[24]. As can be seen in Figure 2-1, monolayer TMD materials in the 2H phase (most common phase, the only studied in this chapter) have a hexagonal crystal form with no centrosymmetry. However, as a bilayer crystal, the crystal has a symmetry point between the two
atomic layers. For odd number of layers, there is no symmetry point, but for even number of layers, a symmetry point arises. This makes the second order nonlinear response of few-layered TMD materials very susceptible to the number of layers, as centrosymmetric materials have a vanishing $\chi^{(2)}$ under the dipole approximation[47].

Figure 2-1 Transition Metal Dichalcogenide Crystal Structure. Left: Monolayer crystal structure. Right: Bilayer crystal structure. Symmetry point between layers is marked.

The TMD materials used in this work were fabricated by collaborators in Prof. Mauricio Terrones group in their lab at the Pennsylvania State University by two separate methods: as exfoliated flakes and as synthesized triangles. Exfoliated flakes are obtained using the method reported in reference [30]. Few-layer crystals were deposited on a contrast enhancing SiO$_2$/Si substrate using the scotch tape method of mechanical exfoliation. This method often leads to crystal flakes with various thicknesses (c.f. Figure 2-4). The synthesized triangles are grown using a two-step process outlined in reference[24]. One-nanometer films of WO$_3$ or MoO$_3$ (99.998% Alfa Aesar) are thermally evaporated onto the contrast enhancement SiO$_2$/Si substrates at 10$^{-6}$ torr. The films are then placed into a quartz reaction chamber and heated next to a boat of Sulfur powder (99.5% Alfa Aesar). The Sulfur was heated to 250°C and the WO$_3$ films were heated to 800°C. The synthesis was
carried out under a 100 sccm Argon flow with atmospheric pressure at the exit of the tube. This leads to synthesis of primarily monolayer triangles, with rarer other crystal orientations as well (c.f. Figure 2-7). To transfer any sample off the SiO$_2$/Si substrates and onto an arbitrary substrate (a TEM grid, a planar cavity, microresonator, etc.), the sample was first spin coated with a PMMA solution (495 000) at 3000 RPM. Once dried overnight, the SiO$_2$ is then etched away from under the polymer/TMD matrix using a KOH 15 M solution. This released the PMMA/TMD film, which was fished out with the new substrate. This was then washed to remove the caustic KOH solution, and acetone was used to remove the PMMA.

Due to their inherent sub-nanometer thickness, it is difficult to determine the difference between layer numbers when dealing with atomically layered materials, and as such, there have been several methods developed to solve this problem. The two most common methods are atomic force microscopy (AFM) [24] and Raman Spectroscopy[23]. Both methods were implemented to verify that the number of layers were well known in all work done with few-layered materials in this dissertation. Literature demonstrates that a single TMD monolayer has a thickness between 0.65 - 0.9nm and bilayers a larger height of approximately 1.3 to 1.6nm[30]. Figure 2-2a demonstrates a MoS$_2$ monolayer AFM topography image done on a SiO$_2$/Si substrate. The measured height along the red line (Figure 2-2b) us approximately 0.8nm, indicating the MoS$_2$ crystal is a monolayer.
Figure 2-2 AFM measurements on Monolayer MoS$_2$. a) Non-contact mode AFM image. b) Measured topographic height along the line in (a). Height measured is a thickness of 0.8nm, indicating the sample is monolayer. AFM scan taken by Simin Feng of Prof. Terrones’ group.

Raman spectroscopy is an alternative method to AFM scanning to determine the number of layers in monolayer crystals, and this has been verified in several recent papers [23, 48]. Monolayer MoS$_2$, for example, shows characteristic E’ and A’$_1$ modes with a frequency difference of approximately 20 cm$^{-1}$. As the number of layers increase, the addition of layers increase the van der Waals and Coulomb interactions; for bilayer MoS$_2$, the E’ and A’$_1$ modes shift to 23cm$^{-1}$ frequency difference. Figure 2-3a demonstrates the Raman spectrum of a MoS$_2$ monolayer on a SiO$_2$/Si substrate. The E’ and A’$_1$ modes are 20 cm$^{-1}$ apart, showing the sample is a monolayer. Furthermore, it has been demonstrated that as the number of layers decreases for TMD samples, the PL signal increases inversely[24]. Figure 2-3b plots the PL and Raman spectrum of a MoS$_2$ sample on a SiO$_2$/Si substrate. It is clear that the PL intensity is much larger than the Raman spectrum, a further indicator that the sample is a monolayer.
2.2 Second Harmonic Generation in Layered TMDs

For a single layer or an odd few-layered crystal, the TMD crystal inversion symmetry gets broken and the crystal has a strong second order nonlinear susceptibility. This can be seen in Figure 2-4, where an exfoliated WSe₂ flake on a SiO₂/Si substrate is scanned for second harmonic generation[30]. Figure 2-4a depicts an optical micrograph of the WSe₂ flake, where regions of four thicknesses can be discerned: bulk (center), three-layer (bottom right), bilayer (bottom), and monolayer (right) regions. The differences in the regions can be better seen in the PL image in fig. 2-4b, where the thinner (mono- and bi-layer) regions emit more PL than the thicker regions. When looking at an SHG raster scan image of the image (fig. 2-4c), it is clear that the monolayer region has the largest susceptibility, followed by the trilayer region. Also apparent, the bilayer region has no SHG signal, demonstrating that the crystal symmetry suppresses the SHG in even number of layers.
Figure 2-4 Exfoliated WSe$_2$ Flake SHG. a) Optical micrograph of WSe$_2$ flake. b) Photoluminescence image of the same WSe$_2$ flake. Stronger PL generation corresponds with a fewer number layered crystal. c) SHG raster scan of the WSe$_2$ flake.
As can be seen in fig. 2-4, the few layered regions of the flake have a strong second harmonic response when compared to the SiO$_2$/Si substrate, which, at an incident average power of 1 mw, is negligible. This leads to the conclusion that monolayer TMDs can have an extraordinary second order nonlinear response, leading them to be excellent materials to coat other materials with low second order susceptibility, such as silicon or glass.

2.3 Calculating the Second Order Nonlinear Susceptibility of Monolayer TMDs

In order to characterize the second-order nonlinear susceptibility of a monolayer TMD crystal, a model was developed with a monolayer TMD crystal on a semi-infinite substrate (Figure 2-5)[25, 31]. An incident plane wave source is focused by a lens (focal length of $F$, aperture radius $a$, and numerical aperture $NA = a/F$) onto the sample, generating the second-order response from the crystal. In this case, as a two-dimensional material, the crystal acts as a Green’s function nonlinear sheet source, where the second harmonic field, $E_2$, can be determined from equation (2.1)

$$\left( \nabla^2 + \frac{\omega^2}{c^2} n^2(z) \right) E_2 = -\mu_0 \varepsilon_0 \omega^2 \hat{e}_2 \cdot \chi^{(2)} : \hat{e}_1 E_1^2$$

(2.1)

where $\omega_2$ is the angular frequency of the second harmonic signal, $c$ is the speed of light in vacuum, and $\mu_0$ is the vacuum permeability, and $\varepsilon_0$ are the vacuum permittivity. As can be seen in Figure 2-5, the sample is located at $z = 0$ surrounded by atmosphere and a semi-infinite substrate; therefore, the refractive index of the surrounding medium, $n(z)$, is $n(z) = 1$ for $z < 0$ and $n(z) = n_2$ for $z > 0$. The fundamental field at the monolayer sheet, $E_1$, is polarized along the vector $\hat{e}_1$, while $E_2$ is polarized along $\hat{e}_2$. $\chi^{(2)}$ is the second order nonlinear susceptibility tensor of the monolayer material. As discussed before, the substrate has negligible SHG in Figure 2-4, so the nonlinear signal emitted from the substrate can be ignored.
Figure 2-5 Model for Monolayer Second Harmonic Generation. Incident plane wave is focused by a lens onto the 2D material, located at z=0. 2D film is fixed atop a semi-infinite substrate with negligible second order nonlinear susceptibility.

Due to the atomic thickness of the TMD monolayer, we can represent the nonlinear polarization of the monolayer as a Dirac delta function, $\delta(z)$. This allows us to represent the nonlinear susceptibility as a nonlinear surface susceptibility, $\chi^{(2)}_s$, i.e. $\hat{e}_2 \cdot \chi^{(2)}_s \hat{e}_1 = \chi^{(2)}_s \delta(z)$.

The fundamental field at the sample, $E_1$, can be represented using the Debye integral[49],

$$E_1(x, y, 0) = \left(\frac{2}{n_{1+1}}\right) \lambda_1 E_o F \int \int circ \left(\frac{\lambda_1 u}{N_A}, \frac{\lambda_1 v}{N_A}\right) e^{i2\pi(xu+yv)} dudv$$

where $E_o$ is the incident field at the aperture of the lens, $n_1$ is the refractive index of the substrate at the fundamental wavelength of $\lambda_1$, and $circ()$ is the circular aperture function of the lens. Using equations (2.1) and (2.2), one can solve for the second harmonic field generated by the nonlinear sheet source:

$$E_2(x, y, z) = \frac{-\omega_2^2 \chi_s^{(2)}}{c^2 \lambda_2^2} e^{-i2\pi\lambda_2^{-1}z} e^{-\frac{i\pi}{\lambda_2^2}(x^2+y^2)} E_1 \left(-\frac{x}{\lambda_2 z}, -\frac{y}{\lambda_2 z}\right) \otimes E_1 \left(-\frac{x}{\lambda_2 z}, -\frac{y}{\lambda_2 z}\right)$$

Solving for the power of the epi-collected SH field, $P_2 = 2\varepsilon_o c \int \int |E_2(x, y, -F)|^2 dxdy$, one can calculate the instantaneous SHG power ($P_2$) generated by the monolayer material as
where $\phi = 8\pi \int_0^1 \cos^{-1} \rho - \rho \sqrt{1 - \rho^2} \rho d\rho \approx 3.56$ is a factor arising from the convolution in equation (2.3). $P_1$ is the peak power of the fundamental field. One note of interest is that the atomic thickness makes monolayer samples excellent platforms for optical pulse characterization due to their inherently wide bandwidth (see section 2.7 for more information).

Using equation (2.4), we can solve for the second order nonlinear sheet susceptibility in terms of average power ($P_{av}$) and pulse repetition rate ($R$):

$$
\chi_s^{(2)} = \frac{32 \pi A^2 \ell_1^2 P_{av}}{N(1+1)^4} R (n_2+1)^2 \frac{P_{av} \phi}{2} 
$$

Once the nonlinear sheet susceptibility in equation (2.5) is determined, one can also calculate the effective bulk susceptibility, $d_{eff} = \chi_s^{(2)} / 2T$, where $T$ is the thickness of the monolayer material.

Using equation (2.5), one can easily represent the nonlinear sheet susceptibility of a monolayer material using simple values measured in experimental conditions. In order to determine the $\chi_s^{(2)}$ for a TMD monolayer, we used a simple microscope system shown in Figure 2.6. The output from a mode-locked Ti-sapphire laser (KM Labs, $\lambda_1 = 830$ nm, R=88MHz, $t_1=106$ fs) is focused onto the sample using a long working distance objective lens (Mitutoyo, 50x, NA=0.55, spot size ~ 1.8 µm). The SH signal is epi-collected with the same lens and reflected off a dichroic beam splitter, filtered, and sent into a spectrometer (PIActon 2500i, liquid nitrogen cooled CCD, integration time of 1 s). The spectrometer was calibrated to a known SHG source, allowing the power of the generated SHG signal to be determined.
Figure 2-6 Schematic of the SHG Experimental Setup. Output from Ti:sapphire laser is focused by at 50x objective lens (OL) onto the sample. SH signal is epi-collected and reflected off a dichroic beamsplitter (DB). Signal is filtered by a 420nm bandpass filter (BP) and detected by a spectrometer (PlActon 2500i).

Using the setup as illustrated in Figure 2-6, the SHG power was measured from monolayer WS$_2$ on SiO$_2$/Si substrates. Figure 2-7a shows an optical image of a representative WS$_2$ triangle, and Figure 2-7b shows a raster scan of the same WS$_2$ triangle. To minimize any effect of the substrate on the measurement, WS$_2$ triangles were also measured suspended on a TEM grid (Quantifoil, from SPI) (Figure 2-7c), where the presence of no substrate will give a more accurate representation of the second order nonlinear susceptibility for monolayer WS$_2$ (Figure 2-7d). A normalized spectrum for both the fundamental and second harmonic signals are plotted in the insert in fig. 2-7e. The results are shown in Figure 2-7e for samples on both SiO$_2$/Si and suspended substrates. The data plotted in log-log form has an approximate slope of 2 (2.04 for SiO$_2$/Si and 2.12 for suspended), and with the spectra shown in the insert of Figure 2-7e, are clear indications that the signal is SHG. Taking the data from Figure 2-7 and using equation (2.5), one can calculate the bulk second order susceptibility for monolayer WS$_2$ as $d_{eff} = 4.51$nm/V for samples on SiO$_2$/Si substrates, and 4.46nm/V for suspended samples[25]. Taking data across several samples on various substrates of each type, there
was a variance of 0.3 nm/V for SiO₂/Si samples and 0.1 nm/V for suspended samples, making the susceptibility values calculated a good representation for monolayer WS₂.

Figure 2-7 SHG measurement of monolayer WS₂. a) Optical micrograph of a WS₂ monolayer on a SiO₂/Si substrate. b) SHG raster scan of the same triangle in (a). c) Optical micrograph of a WS₂ monolayer suspended on a TEM grid. d) SHG raster scan of the WS₂ monolayer in (c). e) Power scan of a WS₂ monolayer on a SiO₂/Si substrate (red) and suspended on a TEM grid (black). Insert shows the fundamental (red) and SH (blue) spectra captured by the spectrometer.

Table 2-1 contains dₑff values for several materials. It can easily be seen that compared to common nonlinear materials, such as BaB₂O₄ (BBO), monolayer TMDs, such as WS₂ and WSe₂ have over 3 orders of magnitude larger second order nonlinear susceptibility.
Table 2.1. Second Order Nonlinear Susceptibility of Various Materials [30]

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>d (nm/V)</th>
<th>λ_1 (nm)</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-SiO\textsubscript{2}</td>
<td>d\textsubscript{11} = 0.4 × 10\textsuperscript{-3}</td>
<td>1058</td>
<td>[50]</td>
</tr>
<tr>
<td>β-BaB\textsubscript{2}O\textsubscript{4}</td>
<td>d\textsubscript{11} = 1.6 × 10\textsuperscript{-3}</td>
<td>1064</td>
<td>[51]</td>
</tr>
<tr>
<td>(9L) GaSe</td>
<td>d\textsubscript{eff} = 9.3 × 10\textsuperscript{-3}</td>
<td>1560</td>
<td>[52]</td>
</tr>
<tr>
<td>3r MoS\textsubscript{2} (bulk)</td>
<td>d\textsubscript{21} = 0.5</td>
<td>1064</td>
<td>[43]</td>
</tr>
<tr>
<td>2h MoS\textsubscript{2} (bulk)</td>
<td>d\textsubscript{eff} &lt; 5 × 10\textsuperscript{-5}</td>
<td>1064</td>
<td>[43]</td>
</tr>
<tr>
<td>H WSe\textsubscript{2}</td>
<td>d\textsubscript{eff} = 5</td>
<td>816</td>
<td>[30]</td>
</tr>
<tr>
<td>H MoS\textsubscript{2}</td>
<td>d\textsubscript{eff} = 5</td>
<td>810</td>
<td>[45]</td>
</tr>
<tr>
<td>H WS\textsubscript{2}</td>
<td>d\textsubscript{eff} = 4.5</td>
<td>832</td>
<td>[25]</td>
</tr>
</tbody>
</table>

Also of important note is the absence of edge-enhancement in the SHG images in Figure 2-7. It has been demonstrated that, in synthesized monolayer MoS\textsubscript{2}, there is significant edge enhancement in the PL generated by the monolayer [24]. This is in stark contrast with the SHG images in Figure 2-7, where the SH signal is very even across both the SiO\textsubscript{2}/Si and TEM grid samples. It is important to note that SHG edge enhancement has been studied, but this has only been demonstrated in monolayer MoS\textsubscript{2} when the fundamental field has a wavelength at twice that of the bandgap wavelength of the material [46]. Because the samples measured in this experiment are far from twice the WS\textsubscript{2} bandgap wavelength (~630nm), the lack of SHG edge enhancement is not unexpected.

### 2.4 Substrate Effect on SHG

As can be seen from fig. 2-7, the power generated by suspended samples is several times that of the monolayer on SiO\textsubscript{2}/Si substrates. Furthermore, in the suspended WS\textsubscript{2} SHG image, there is significant pattern in the SH signal generated. Both of these arise from a change in the refractive index of the substrate. n\textsubscript{1} and n\textsubscript{2} are significantly more for SiO\textsubscript{2}/Si substrates than suspended samples, and following equation (2.4), the SH power is decreased. However, due to the atomic thickness of monolayer materials, contrast enhancement substrates, such as the SiO\textsubscript{2}/Si substrate used in Figure 2-7, are often employed to increase the contrast of the 2D films [53]. Therefore, the model described in...
section 2.3 utilizing a semi-infinite substrate is not an exact model for contrast enhancement substrates. Therefore, the susceptibility calculated with equation (2.5) should be adjusted accordingly[31].

![Figure 2-8 SiO$_2$/Si Fabry-Perot Cavity Model. a) 2D/SiO$_2$/Si sample used in this experiment. b) Asymmetric Fabry-Perot cavity in the 2D/SiO$_2$ cavity. c) Asymmetric Fabry-Perot cavity of the oxide layer. The cavity in (b) creates a complex reflection/transmission coefficient at one side of the SiO$_2$ interface.]

As can be seen from Figure 2-8a, the contrast enhancement substrate differs from the air/2D/semi-infinite substrate model by forming an extra interface as air/2D/SiO$_2$/Si interface. In order to determine the effect of the cavity formed, we use an asymmetric Fabry-Perot model to account for both the 2D/SiO$_2$ and SiO$_2$/Si interfaces. An asymmetric Fabry-Perot cavity has a reflection coefficient, $r$, of[2]

$$r = r_1 + \frac{t_1' t_2' r_2' e^{-i\delta}}{1 - r_1' r_2' e^{-i\delta}}$$  \hspace{1cm} (2.6)$$

where $r_i$ and $t_i$ are the reflection and transmission coefficients for the first interface ($i=1$) and second interface ($i=2$)[49]. $\delta = 4\pi d n \lambda^{-1}$ is the round trip phase delay. Primed coefficients indicate values from the perspective inside the cavity. Similarly, the transmission coefficient, $t$, can be obtained as

$$t = \frac{t_1' t_2' r_2' e^{-i\delta}}{1 - r_1' r_2' e^{-i\delta}}$$  \hspace{1cm} (2.7)$$
Using these coefficients, we first model the monolayer material as an asymmetric cavity with reflection coefficients $r_{1}^{2D}$ and $t_{1}^{2D}$. This becomes the reflection coefficients $r_{1}$ and $t_{1}$ for the oxide layer cavity. Using equations (2.6) and (2.7), one can determine the corrected susceptibility, $\tilde{\chi}_s^{(2)}$, as

$$\tilde{\chi}_s^{(2)} = \frac{1}{\eta_1 \eta_2} \chi_s^{(2)}$$

(2.8)

where $\eta_1$ is the fundamental field enhancement, $\eta_2$ is the SH field enhancement, and $\chi_s^{(2)}$ is the value determined in equation (2.5). When considering the 285nm oxide contrast enhancement substrates used in Figure 2.7, $\chi_s^{(2)}$ is overestimated by as much as 15%. However, this correction only accounts for normally incident fields and not a decomposition of the full angular spectrum. A full decomposition of the cavity effect is discussed in reference [54], including nonlinear Kerr effects for higher power pump excitation. Therefore, due to the complexity of modeling this approach (similar to the chapter 4 absorption model), the susceptibility measured from the suspended samples provides a more accurate estimate of monolayer WS$_2$’s second nonlinear susceptibility.

### 2.5 Density Functional Theory Calculation of Monolayer TMDs

As seen in table 2.1, monolayer TMDs have an extraordinarily high second order nonlinear susceptibility. To understand the origin of this value, the nonlinear susceptibility can be calculated using Density Functional Theory (DFT) simulations. These calculations were performed by our collaborators in Prof. Vincent Crespi’s group at the Pennsylvania State University. Using the band structure of monolayer WS$_2$ (Figure 2-9a), reference [25] calculates the second order nonlinear susceptibility using an ABINIT software package (Figure2-9b)[55, 56, 57, 58, 59]. As can be seen in Figure 2-9b, the second order nonlinear susceptibility is influenced by an increased joint density of states (JDOS), the shaded regions on the bottom of Figure 2-9b. These correlate to the shaded regions in Figure 2-9a, where the highest valence and the second conduction band are locally parallel. This leads to the conclusion that the large nonlinear susceptibility is due to resonance enhancement and the
JDOS enhancement arising in monolayer WS$_2$. Furthermore, the second order transition ‘V’ is strongly enhanced due to the presence of transition ‘I’ at the half-way point in energy. This resonance enhancement and increased JDOS both lead to a large increase in the susceptibility. As can be seen in Figure 2-9b, at $\lambda_1 = 830$nm (1.49eV), $\chi^{(2)} \approx 0.5\text{nm/V}$ for monolayer WS$_2$. When averaged across the simulation cell height, ref. [25] determines that monolayer WS$_2$ has $d_{eff} = 0.77\text{nm/V}$. Considering that quasiparticle and exitonic effects are ignored, this is a very good order of magnitude agreement to the value calculated in section 2.3.

From Figure 2-9b it is apparent that at our pump wavelength of $\lambda = 830$nm (1.49 eV), there is a strong increase in the SH response of WS$_2$. Furthermore, it is apparent that the SH signal generated by monolayer WS$_2$ varies significantly due to the enhancement inherent in the bands of the crystal, as seen in Figure 2-9a. Other 2D TMD materials, having different band structures, will have different SH responses, as can be seen in Table 2-1. Due to the ability to fabricate TMD monolayer alloys[33], it is possible to engineer the second order nonlinear response of the monolayer. This will be the focus of chapter 3, where it is demonstrated that by varying the composition of the monolayer alloy, one can generate a different second order nonlinear response.
Figure 2-9 DFT Susceptibility Theoretical Calculation. a) Band structure for monolayer WS$_2$. The parallel bands shaded near transition ‘II’ and ‘IV’ give rise to an increased JDOS, and region ‘V’ is enhanced from a half-way transition ‘I’. b) Nonlinear susceptibility of monolayer WS$_2$. Also shown are the JDOS contributions from the first three conduction bands aligned to the regions indicated in (a). DFT calculations were performed by Y. Wang.
2.6 TMD Polarized SHG Response for Monolayer TMDs

Until this point, we have ignored the tensorial property of the second order nonlinear susceptibility. As can be seen in equation (2.1), the output of the SH signal is highly dependent on the polarization of the fundamental field in relation to the crystal axis. Due to the hexagonal P6/mmc crystal symmetry, the nonlinear susceptibility tensor has nonzero elements at \( d_{yxy} = -d_{yxx} = -d_{xyx} \), where \( x \) and \( y \) represent the crystal axes[47]. This leads to an effective nonlinear polarizability \( (p^{NL}) \) matrix, of

\[
\begin{bmatrix}
    p_x^{NL}(2\omega) \\
p_y^{NL}(2\omega) \\
p_z^{NL}(2\omega)
\end{bmatrix} =
\begin{bmatrix}
    0 & 0 & 0 & 0 & -d \\
    -d & d & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
    E_x^2(\omega) \\
    E_y^2(\omega) \\
    E_z^2(\omega) \\
    E_y(\omega)E_x(\omega) \\
    E_x(\omega)E_y(\omega)
\end{bmatrix}
\]  

(2.9)

Because \( p^{NL} = p_x^{NL} \cos \theta + p_y^{NL} \sin \theta \), where \( \theta \) is the angle between the mirror plane and the incident polarization, this results in a SH signal power with a \( P_2 \propto |p^{NL}|^2 \propto \cos^2 3\theta \) relationship. This can easily be seen in Figure 2-10, where the polarized SH signal generated by the monolayer region in figure 2-4 is plotted against the \( \cos^2 3\theta \) fit.
To measure the polarization response from the monolayer, the measurement setup was slightly modified as represented in Figure 2-11 (see changes in reference to Figure 2-6). The fundamental field was first made circularly polarized to allow access to any linear polarization. Then, a polarizer was mounted in a rotational stage and placed between the dichroic beamsplitter and the lens. By rotating the polarizer, the incident field’s polarization was rotated accordingly. Therefore, not only is the incident field polarization rotated, but the SH field detected by the spectrometer is also polarized along the axis of the polarizer. This allows for the detection of the SH field along the same axis as well.
Using this system, we can then utilize the tensorial properties of the second order nonlinear susceptibility to probe crystal symmetry and crystal axis orientation. Figure 2-12 shows two WS$_2$ triangles on a SiO$_2$/Si substrate. In Figure 2-12, a SHG raster scan is shown along with its polarized SHG response on the left. In contrast, the triangle on the right has been rotated approximately 18 degrees in reference to the left triangle. When looking at the polarized SHG response of the second triangle, the SHG rotation is also 18 degrees, demonstrating that SHG is an effective tool in probing the symmetry and crystal axis of monolayer TMDs. (Note: this technique was recently utilized in determining grain boundaries in large-scale MoS$_2$ films in reference[46]).
2.7 Frequency Resolved Optical Gating using Monolayer TMDs

There are other advantages when generating SHG signal with ultra-short laser pulses from ultra-thin materials. Due to the atomic thickness of monolayer TMD materials, it has incredibly high spatial resolution, making it excellent for spatially resolved applications, such as optical in situ pulse characterization directly at a lens focal point. Furthermore, it is often crucial to characterize an ultra-short laser pulse for evaluating laser performance[60], for quantum coherence control[61], and for complex spectroscopic applications[62]. Even when characterizing the second order nonlinear susceptibility of a material, such as in section 2.3, it is crucial to have precise knowledge of the fundamental pulse (c.f. equation 2.5). Due to their atomic thickness, monolayer TMDs have an inherently wide phase matching bandwidth and relaxed phase matching requirements. This, and its extraordinarily high second order nonlinear susceptibility, make 2D TMDs excellent materials to perform ultrafast pulse analysis in the form of SHG frequency resolved optical gating, (SHG-FROG). SHG-FROG is a common technique to characterize complex and ultra-short optical pulses. By
measuring the spectrally resolved auto-correlation trace, known as a spectrogram, and implementing a phase retrieval algorithm, SHG-FROG can retrieve the amplitude and phase of any arbitrary ultra-short optical pulse. In this section, monolayer WS$_2$ pulses will be applied to characterize optical pulses through the use of SHG-cFROG.

SHG-cFROG utilizes two separate copies of the optical pulse collinearly propagating through the 2D material. These pulses are the original, $E(t)$, and a copy delayed by time $\tau$, $E(t-\tau)$. Therefore, the SH field is generated by the total field is proportional to $(E_1(t) + E_1(t-\tau))^2$. Thus, the intensity of the SH field measured for the spectrogram is proportional to the square of the Fourier Transform of the new field,

$$I_{cFROG}(\omega, \tau) \propto \left| F.T. \left\{ (E_1(t) + E_1(t-\tau))^2 \right\} \right|^2 = 2I_{SH}(\omega) + 4I_{FROG}(\omega, \tau) + \cdots$$  (2.10)

where $I_{SH}(\omega)$ and $I_{FROG}(\omega, \tau)$ are the background SH spectrum and standard non-collinear FROG spectrum, respectively\[63\]. The ellipsis indicates the presence of other terms, however these are removed by the digital filtering of the spectrogram.

It is important to note that this conclusion is limited by the group velocity mismatch (GVM) of the fundamental and second harmonic fields\[64\]. In bulk nonlinear crystals, the fundamental and SH fields will propagate at different group velocities due to the dispersion effect, resulting in a restricted bandwidth. With these traditional crystals, methods such as angle-dithering have been utilized to remove the problems from GVM. In order to see the importance of crystal thickness on the phase matching bandwidth, we look at the optical wave equation derived from Maxwell’s equations\[47\]:

$$\nabla^2 \mathcal{E} - \mu_o \epsilon_o \frac{\partial^2 \mathcal{E}}{\partial t^2} - \mu_o \frac{\partial^2 \mathcal{P}}{\partial t^2} = 0$$  (2.11)

where $\mathcal{E} = Ae^{-i(\omega t - k z)}$ is the electric field and $\mathcal{P}$ is the polarization, which can be broken down into linear, $\mathcal{P}_L$, and nonlinear, $\mathcal{P}_{NL}$, components. Assuming the slowly-varying envelope approximation and solving for the SH wave, equation (2.11) simplifies to
where \( k_j = 2\pi n_j/\lambda_j \) is the wavevector and \( v_{gj} \) is the group velocity (at wavelength \( j = 1 \) for the fundamental field and \( j = 2 \) for the SH field). We can further simplify this relationship using the undepleted/unperturbed pump assumption, such that \( A_1(z,t) = f(t - z/v_{g1}) \). This looks at the variation of the pulse from the perspective of traveling with the pulse, so that \( \tau = t - z/v_{g1} \). Substituting in equation (2.12) and taking the Fourier Transform (F.T.) of the pulse to determine its bandwidth results in the following relationship.

\[
\frac{\partial A_2}{\partial z} - i\Omega \left( \frac{1}{v_{g2}} - \frac{1}{v_{g1}} \right) \tilde{A}_2 \approx \frac{i\omega_2}{2cn_2} \chi^{(2)} F.T. \left[ A_1^2(\tau) \right] e^{i(2k_1 - k_2)z} \tag{2.13}
\]

where \( \tilde{A} \) is the Fourier Transform of the field amplitude and \( \Omega \) is the angular frequency. To simplify notation, the following variable substitutions will be made from here: \( S(\Omega) = F.T. [A_1^2(\tau)] \) is the Fourier Transform of the square of the slowly varying fundamental pulse, \( \Delta k = 2k_1 - k_2 \) is the wavenumber mismatch, and \( \delta = \frac{1}{v_{g1}} - \frac{1}{v_{g2}} \) is the GVM parameter. Note that the group velocity dispersion, GVD, is not accounted for in this model. Making these substitutions into equation (2.13) and rearranging, we arrive at the following equation.

\[
\tilde{A}_2 \approx i\frac{\omega_2 e^{-i\Omega \delta z}}{2cn_2} \chi^{(2)} S(\Omega)L \text{sinc} \left( \frac{\Delta k - \Omega \delta}{2\pi} L \right) e^{i(\Delta k - \Omega \delta)L/2} \propto S(\Omega) \text{sinc} \left( \frac{\Delta k - \Omega \delta}{2\pi} L \right) \tag{2.14}
\]

where \( L \) is the thickness of the material. From equation (2.14), it is clear to see the effect of \( L \) on the phase bandwidth. When assuming the phase matching condition is met at the central frequency (\( \Delta k = 0 \)), the spectrum is proportional to \( \text{sinc} \left( \frac{\Omega \delta L}{2\pi} \right) \), which effectively filters the signal as a low pass filter with a bandwidth approximately \( (L\delta)^{-1} \). This bandwidth is inversely proportional to the walk-off time between the fundamental and SH pulses. A FROG spectrum taken under a thick crystal is effectively low pass filtered and the pulse profile cannot faithfully be retrieved. This demonstrates the advantage of using monolayer TMD crystals as SHG FROG crystals. Not only do they have an
extraordinarily large nonlinear susceptibility, but, due their atomic thickness (L ~ 0.7nm) also have a very large bandwidth. This makes them excellent materials to characterize broadband or complex pulses.

To measure the spectrogram from a monolayer WS₂ sample, a modification was made to the experimental setup (Figure 2-13). The output from the femtosecond Ti:sapphire is directed into a Michelson interferometer formed by a beamsplitter and two mirrors. One mirror is mounted on a computer-controlled linear translational stage delayed by time τ in order to form the spectrogram. The output of the interferometer is then sent into a similar microscope as in Figure 2-6, focused by a long working distance objective (Mitutoyo 50x, NA=0.55). The epi-collected signal is then reflected off a dichroic beamsplitter before being filtered and directed into a spectrometer (PI Acton, 2500i, 1200grove/mm grating, liquid nitrogen cooled CCD camera, integration time 300ms).

Figure 2-13 Experimental Diagram of the SHG-cFROG Experiment. Output from the Ti:sapphire laser is directed into a Michelson interferometer formed by a beamsplitter (BS) with one arm delayed by time τ. The output is then focused by at 50x objective lens (OL) onto the sample. SH signal is epi-collected and reflected off a dichroic beamsplitter (DB). Signal is filtered by a 420nm bandpass filter (BP) and detected by a spectrometer (PI Acton 2500i).
A representative spectrograph using 0.66 fs delay step size is depicted below in Figure 2-14a, and an interferometric autocorrelation taken from summing along the y-axis is shown in the insert. One can see the presence of both the terms in equation (2.10), and by averaging several marginal delay columns one can remove the SH background to reveal the I_{FROG} term. Figure 2-14b shows the comparison between the FROG spectrogram extracted from the measured data and that of the computed retrieved pulse[65]. Both spectrum are in good comparison and agree well with each other. The amplitude and phase profile of the retrieved pulse are plotted in Figure 2-14c. It can be seen that the pulse width is approximately 106 fs, and furthermore, there is significant chirp in the pulse, most likely due to uncompensated laser cavity dispersion as well as the external optical components of the measurement setup. To further verify the calculated pulse profile, Figure 2-14d compares the spectrum of the computed pulse and the measured spectrum. There is also an excellent match between these spectral profiles, further validating the pulse characterization.

It is important to note the FROG retrieval below assumes that the material generating the SHG signal has a constant nonlinear susceptibility. As can be seen in Figure 2-9, this is not the case for WS\textsubscript{2} monolayers. Although the susceptibility is fairly constant across the bandwidth of the laser pulse retrieved above, if broadband spectra are to be retrieved, the peaks in the susceptibility will be a problem in the retrieval. In order to improve the promise for 2D materials in optical pulse characterization, these peaks will need to be compensated for. One method for doing this is described in chapter 3, where by varying the chemistry of the monolayer material, the peaks in the susceptibility spectra can be suppressed.
In summary, it has been demonstrated that monolayer TMD crystals have extraordinarily strong second harmonic generation. Through their non-vanishing second order nonlinear susceptibility, TMDs have very strong SHG for odd number of layers and a vanishing SHG signal for centrosymmetric even layers. By modeling the monolayer as a Green’s function nonlinear sheet source, an equation was derived containing terms known from the experimental design, allowing the second order nonlinear susceptibility to be calculated. However, due to the contrast enhancement SiO₂/Si substrates and the formation of an asymmetric Fabry-Perot cavity, the calculated value should be corrected. This leads to a more exact estimate when using a suspended sample, leading to a measured value of approximately $d_{\text{eff}} = 4.5 \text{nm/V}$ for monolayer WS₂. This high nonlinear
susceptibility was determined to arise from the resonance enhancement in the crystal band structure, as well as an increased JDOS. Despite the approximations involved with the measured and the DFT model, a calculated value of $d_{\text{eff}} = 0.77 \text{ nm/V}$ was calculated, providing an order of magnitude verification to the measured value.

Furthermore, several applications were demonstrated for the monolayer SHG. Firstly, the large contrast between layer numbers makes SHG imaging an effective tool when trying to image monolayer TMDs. Secondly, when probing for polarized SHG, the crystal symmetry and orientation can be interrogated, making polarized SHG an effective method to probed monolayer crystal orientation without damaging the samples. Additionally, due to their atomic thickness, monolayer TMDs provide an excellent platform for optical pulse characterization. Not only do monolayer TMDs have extraordinarily high susceptibility, but their inherently wide phase matching bandwidth makes them excellent candidates for optical pulse characterization. Furthermore, with the new methods to engineer the band structure of the material by varying the doping level of alloyed TMD, there are opportunities to engineer the susceptibility of the material. This will be further explored in the next chapter.
Chapter 3

Tuning the Second Order Optical Nonlinearity in Monolayer TMDs

In chapter 2, it was demonstrated that monolayer TMD materials are excellent materials for second harmonic generation due to their inherent atomic thickness providing excellent phase-matching bandwidth, and resonant SHG enhancement. These advantages make 2D materials excellent materials to incorporate into nonlinear optical systems. 2D materials have recently been demonstrated to exhibit flexibility when fabricating TMD alloy compositions, demonstrating new optical properties with enhanced PL spectra and multiple Raman peaks [66, 33]. This is an exciting development, as the new alloy compositions could be easily engineered to have a broad range of band gaps and emission spectra. As demonstrated in chapter 2, these changes in band structure lead to the extraordinary nonlinear generation in 2D materials, meaning that by changing the doping concentration within the alloy, the nonlinear response of the material could also be engineered. This can be a challenge for traditional nonlinear crystals, which often have difficulty tuning their inherent second order nonlinear susceptibility [67], requiring advanced techniques, such as polling [68], or advanced materials, such as liquid crystals [69], to tune their nonlinearity.

To demonstrate this, we propose that we can tune the nonlinear susceptibility of 2D materials by varying their alloy doping concentration. In this chapter, we demonstrate that different TMD crystals do have different second order nonlinear spectra through Sum-Frequency Generation (SFG). By mixing a femtosecond pump with white-light supercontinuum, the SFG spectrum of the TMD monolayer can be probed. This provides an alternative characterization of the capability to engineer the nonlinear spectra than SHG, which requires a tunable pump to effectively demonstrate the changes in the nonlinear susceptibility. A W \(_x\)Mo\(_{1-x}\)S\(_2\) alloy is then fabricated and the concentration characterized before measuring the SFG spectrum from the alloy. Finally, by comparing the SFG spectra of the alloy to the pure WS\(_2\) and MoS\(_2\) crystals, we reveal that by varying the concentration of
the alloy, the SFG spectra can be changed to reflect components in the pure material’s nonlinear spectrum. This makes 2D TMD materials excellent materials for optical nonlinear devices, as not only do they have a large phase-matching bandwidth and extraordinary nonlinear enhancement, but by varying the concentration, we can engineer the nonlinear spectrum of the material, which could lead to new applications[32].

3.1 Sum Frequency Generation in Monolayer TMDs

In chapter 2, we discussed the SHG response of TMD monolayers based on the second order polarizability of the material from twice the fundamental pump’s frequency 

\[ p^{NL}(2\omega_1) = \varepsilon_0 \chi^{(2)}(2\omega_1; \omega_1, \omega_1)E(\omega_1)E(\omega_1) \].

In this chapter, we expand this definition and utilize SFG to measure the nonlinear spectrum of the TMD monolayer. The SFG polarizability relationship is seen below in equation (3.1)[47]:

\[ p^{NL}(\omega_1 + \omega_2) = \varepsilon_0 \chi^{(2)}(\omega_1 + \omega_2; \omega_1, \omega_2)E(\omega_1)E(\omega_2) \]  \hspace{1cm} (3.1)

where \( p^{NL} \) is the nonlinear polarization, \( \chi^{(2)} \) is the second order nonlinear susceptibility, \( E \) is the electric field, \( \omega_1 \) and \( \omega_2 \) are the two pump frequencies, and \( \omega_1 + \omega_2 \) is the SFG frequency. Because of the dual wavelength dependence of SFG, it can probe two transitions in a material, and is a common tool in vibrational spectroscopy and imaging[50, 70]. However, it is also a useful tool for characterizing the nonlinear spectrum of a material; when tuning the pump wavelengths [71] or using a supercontinuum source[72], SFG can become a useful tool for mapping the second order nonlinear properties of a material.

In order to measure the SFG spectrum from the 2D layer, we utilize a dual pump system with spectra shown in Figure 3-1. To measure the spectrum of the 2D material, we generate the SFG spectrum by using a femtosecond pump and a white light supercontinuum. This generates the SFG signal at wavelengths calculated by equation (3.2):
where $\lambda_p$ is the femtosecond pump ($\lambda \sim 790\text{nm}$) and $\lambda_c$ is the supercontinuum (500nm – 1200nm, however, the continuum is filtered down to contain primarily 700nm – 1100nm wavelengths, minimizing absorption in the 2D material). Using equation (3.1) and equation (3.2) and the spectra shown in Figure 3-1, these two pumps can generate SFG signals between $370\text{nm} < \lambda_{SFG} < 460\text{nm}$, effectively mapping out the SFG spectrum generated by the 2D material within this region.

\[
\lambda_{SFG} = \left(\frac{1}{\lambda_p} + \frac{1}{\lambda_c}\right)^{-1}
\]

Figure 3-1 Fundamental Pump and a Typical Supercontinuum Spectra

The microscope used to generate the SFG signals is shown in Figure 3-2. The output from a Ti:sapphire laser (Spectra-Physics Tsunami, $\lambda \sim 790\text{nm}$, $\tau \sim 100\text{fs}$, 100MHz repetition rate, 800mW average power) is split using a beam splitter. The majority of the power is sent to generate the supercontinuum signal in a photonic crystal fiber (Newport, FemtoWhite), whose spectra is shown as the blue curve in Figure 3-1. The continuum is then filtered using a 570nm longpass filter to remove most of the pump shorter than the 2D material’s band gap wavelength; this is done to preserve sample integrity when under characterization (power ~ 10mW). The remaining fs pump (~20mW) is sent into a delay line so that the fs pulse and supercontinuum pulse can be matched in time. Both beams are recombined using a 50/50 beamsplitter (Chroma 21000) before directed to the sample (each with ~10mW average power). The two pumps are focused onto the sample with a 60x objective lens.
The epi-collected SFG signal is then reflected using a dichroic mirror before being filtered with a short pass filter (Chroma ET470sp) and detected by a spectrometer (PI Acton 2500i with a liquid nitrogen cooled CCD detector).

Figure 3-2 Schematic of SFG Microscope Experimental Setup. The output from a Ti:sapphire laser is split with a beamsplitter (BS). The transmitted signal is focused through a 20x objective lens (CL 1) and into a photonic crystal fiber (PCF). The supercontinuum light is then collimated by another 20x objective lens (CL 2) before being filtered with a 570nm longpass filter (CF). This light is then recombined with the remaining pump using a 50/50 beamsplitter and then focused onto the sample with a 60x objective lens (OL). The epi-collected signal is then reflected with a dichroic beamsplitter (DB) before filtered with a shortpass filter (SP) and then detected by a spectrometer.

The signal generated by a WS₂ TMD monolayer is plotted as the red curve in Figure 3-3. The large signal at 395nm is the SHG signal generated from the fs pump. This can be seen when the continuum pump is blocked and the signal still remains (yellow curve, 0.1s integration time). The remaining signal is the SFG spectrum generated by both the fs and continuum pumps. To demonstrate that this is SFG and not from the supercontinuum, the pump was blocked and the signal disappeared (blue curve, 10s integration). It is apparent that the WS₂ monolayer has strong SFG generation, with strong SFG signals between 400nm and 460nm.
In order to determine the nonlinear susceptibility spectrum from the SFG signal shown in Figure 3-3, the signal needs to be normalized to the supercontinuum spectra matched with the fs pump pulse. Because the supercontinuum pulse is complex in time, and does not have a flat spectrum, as can be seen in Figure 3-1, the SFG signal generated should be compared to a reference SFG signal with a flat nonlinear susceptibility spectrum, thus removing the dependence the supercontinuum amplitude on the generated SFG signal (equation (3.1)). In this case, we compare the WS$_2$ SFG spectra to the SFG spectrum generated by a Beta Barium Borate (BBO) crystal ($\beta$ phase, 5mm thick crystal). This method has been demonstrated with other crystals, such as quartz, to remove pump effects from SHG/SFG spectrum[45]. Figure 3-4 plots the WS$_2$ SFG spectrum normalized to the BBO SFG spectrum ($I_{WS_2}/I_{BBO}$). As can be seen in the figure, the SHG signal is much larger than that of the BBO, and the region between 400nm and 410nm has increased SFG above the BBO spectrum. This may be indicative of the SHG enhancement peak located at 1.5eV (c.f. Figure 2-9). The remaining portion of the SFG spectra is fairly uniform. The signal longer than
450nm has much lower intensity than the remaining spectra (see Figure 3-3), thus the normalized spectrum varies much more significantly due to poorer signal-to-noise ratio.

![Graph](image_url)

Figure 3-4 WS\textsubscript{2} SFG Spectrum Normalized to BBO SFG Spectrum

### 3.2 Engineering the Second Order Susceptibility in Monolayer TMDs

As was presented in chapter 2, the nonlinear susceptibility of monolayer WS\textsubscript{2} was calculated by our collaborators using DFT methods. From the results presented in section 2.5, it was apparent that the enhanced SHG response was due to enhanced JDOS and presence of resonant band transitions through the band structure. This makes the second order nonlinear response of monolayer TMDs susceptible to changes in the band structure of the crystal. Although similar, the band structure for monolayer MoS\textsubscript{2} and WS\textsubscript{2} are different as shown in Figure 3-5.
Thus far, we have demonstrated that SFG can be used to effectively probe the second order nonlinear susceptibility of monolayer materials. But as shown in section 2.5 (Figure 2-9), the spectrum is highly dependent on the band structure of the TMD material. From the band structure above, it can be seen that there are several slight differences in the band structure between the two materials. This allows the SFG spectra of the TMD material to be highly dependent on the composition of the 2D layer. This is an interesting factor for TMD alloys, as the composition can be easily varied to form various alloys and heterostructures[33].

In order to demonstrate the capability to engineer new nonlinear spectra, we first look at the nonlinear susceptibility spectrum differences between the two monolayer TMD materials in the alloy $W_xMo_{1-x}S_2$: WS$_2$ and MoS$_2$. The SFG signals normalized to the BBO reference are shown in Figure 3-6. The WS$_2$ (blue) signal has a much stronger SHG signal than the MoS$_2$ (yellow). This is seen in current literature, where WS$_2$ SHG is several times larger than the MoS$_2$ SHG signal at 800nm pump[45], and this increase in the WS$_2$ susceptibility could arise from the peak in WS$_2$ found in our SHG calculation around 1.5eV (c.f. Figure 2-9), where there is a significant increase in the

![Band Structures of Monolayer MoS$_2$ and WS$_2$. Areas of resonant band transitions and enhanced JDOS are the labeled transitions. Calculated by Y. Wang.](image-url)
susceptibility. Also, the WS\textsubscript{2} SFG signal has more enhancement in the range below 410nm, where the SFG values are several times larger than that of the BBO. In this range, the MoS\textsubscript{2} has much less enhancement, with values comparable to that of the BBO. For the range between 415nm and 450nm, the SFG spectra for both the WS\textsubscript{2} and MoS\textsubscript{2} are comparable.

Figure 3-6 SFG Spectra from WS\textsubscript{2}, MoS\textsubscript{2}, and W\textsubscript{x}Mo\textsubscript{1-x}S\textsubscript{2} Alloy. Insert shows increased resolution across the SFG peaks.

In order to demonstrate the ability to engineer the nonlinear susceptibility of the materials, a W\textsubscript{x}Mo\textsubscript{1-x}S\textsubscript{2} alloy was fabricated using the methods described in reference [33]. An optical micrograph of the alloy is shown in Figure 3-7a. The Raman spectra is shown in Figure 3-7b, taken along the dashed line in Figure 3-7a. The Raman modes for WS\textsubscript{2} and MoS\textsubscript{2} are shown below the figure. It is apparent that there is much more WS\textsubscript{2} Raman signal towards the edges of the layer and increasing MoS\textsubscript{2} Raman peaks towards the center of the alloy, leading to the conclusion that the edges are more pure WS\textsubscript{2} and the center contains more alloy composition. To determine the actual concentration, we look at the PL generated by the layer, plotted in Figure 3-7c. Pure WS\textsubscript{2} has a PL
peak centered at 1.97eV and MoS\textsubscript{2} has the peak centered at 1.81eV. By using the shift of the PL peak, we use equation (3.3) to determine the alloy composition\cite{33}:

$$E_{\text{alloy}} = (1 - x)E_{\text{MoS}_2} + xE_{\text{WS}_2} - 0.25x(1 - x)$$  \hspace{1cm} (3.3)

where E is the center of the according PL peak and x is the concentration of W. Using equation (3.3), the calculated concentration of W is shown in Figure 3-7d. From this, we can see that the edges of the alloy do indeed have a higher W concentration (~90%) while the center has an alloy concentration of approximately 56% W and 44% Mo.
Figure 3-7 $W_{x}Mo_{1-x}S_{2}$ Alloy. a) Optical micrograph of the alloy monolayer. b) Raman spectra taken from the alloy along the dashed line in (a). Raman peaks are labeled below the figure. c) PL peaks taken along the dashed line in (a). d) Band gap and W concentration calculated along the dashed line in (a). Data provided by Z. Lin.
Figure 3-8 below shows the SFG spectrum taken along the dashed line in Figure 3-7a. The SHG signal dominates the SFG spectrum, making it barely visible. Therefore, Figure 3-8b shows the same plot as Figure 3-8a, but at a different scale. It is very apparent that the SFG spectrum varies as the concentration changes (edges vs. center), especially in the 400nm to 410nm range. This is very similar to the range where pure WS$_2$ and MoS$_2$ differ in Figure 3-6. To better show this, the SFG spectra of a W rich (edge, 85% W) and a more even alloy concentration (layer center, 55% W, 45% Mo) are also plotted in Figure 3-6. It is very apparent that the W rich edge areas are much more similar to the pure W sample, and the center region has components of both the pure MoS$_2$ and WS$_2$ spectra.

Figure 3-8 SFG Spectra from W$_x$Mo$_{1-x}$S$_2$ Alloy. a) SFG spectrum at full scale, showing primarily the SHG signal. b) SFG spectrum at reduced scale to reveal SFG spectra.

Figure 3-8 efficiently demonstrates the ability to engineer the nonlinear susceptibility of 2D monolayers. By varying the concentration of the W and Mo atoms, which can be easily controlled during the fabrication process, the nonlinear susceptibility can be tuned to exhibit properties of either’s SFG spectra. This effectively allows the engineering of the nonlinear susceptibility of any TMD layer. By tuning the composition of the atoms during the fabrication process, the nonlinear spectrum of the material can be tuned to exhibit properties similar to their original composition.
Although the nonlinear spectra is not a linear composition of the pure SFG spectra due to complicated resonances within the newly formed bands, the SFG spectra could be calculated using DFT theory. Altogether, this makes 2D TMD monolayers an excellent platform for nonlinear devices and applications. Not only can it have exceptionally large susceptibility enhancement, but by varying the concentration, the susceptibility can be engineered to match desired qualifications.
Chapter 4

Nanocavity Enhancement of Light Interaction with Monolayer TMDs

Although the atomically thin form of monolayer TMDs opens up the unique properties of a direct bandgap and extraordinary nonlinear susceptibility, the ultra-thin layer can become critical problem for optical absorption based devices[73, 74]. Due to the inherent atomic thickness in monolayer materials, 2D materials cannot absorb much of the incident light; graphene for example, has approximately 2.3% absorption for a free standing monolayer[75]. The advantages utilized in chapters 2 and 3 for nonlinear generation, become a great disadvantage when engineering devices based on utilizing the 2D films for absorption or photoluminescence. While this low absorption may be beneficial for some optical devices, for other devices, such as solar cells[76], photodetectors[77, 78], and light sources[79, 80], this becomes a critical problem to overcome. Overcoming these light-matter interaction limitations has become a focus of much research, developing methods such as multi-layered cavity structures[81], prism-coupled total internal reflection systems[82], photonic crystal cavities[83], or whispering gallery microdisks[38]. Many of these enhancement strategies, especially those based off Fabry-Perot cavities, rely on placing the film inside the structure, thus limiting the ability for the 2D material to interact with external media. These present challenges for some applications, such a photocatalysts or sensing applications where contact with the film is required[84].

In this chapter, a planar nanocavity design is presented to enhance the light-matter interaction of a monolayer MoS$_2$ crystal while allowing the crystal to be exposed to external media[34]. The nanocavity design, composed of a MoS$_2$ monolayer, alumina spacer, and an aluminum reflector, can be tailored to specific resonant wavelengths by tuning the tens-of-nanometer thick oxide spacer layer.
While the bottom metal reflector reflects most of the light within the cavity, the MoS$_2$ layer partially reflects the light at the top layer with a phase shift, creating a cavity. Although this cavity has a low-Q factor, almost all of the absorption occurs in the MoS$_2$ monolayer, which is not the case when using SiO$_2$/Si contrast enhancement substrates, where significant absorption occurs in the SiO$_2$/Si interface. Furthermore, by placing the MoS$_2$ layer in this cavity, the layer is exposed to its own reflected field from the nanocavity, modifying its spontaneous emission rate. This emission rate can also be tuned by varying the thickness of the oxide spacer layer, granting further design flexibility for optical emission devices.

4.1 Optical Absorption in Monolayer TMDs

The single-pass optical absorption of a monolayer is relatively weak, primarily due to the sub-nanometer thickness of the material. As light propagates through a material, the optical intensity attenuated exponentially according to Beer’s law, $I = I_0 e^{-4\pi\kappa d/\lambda}$[85]. $I_0$ is the initial field intensity, $\lambda$ is the wavelength, $\kappa$ is the imaginary component of the refractive index, and $d$ is the material thickness. For a MoS$_2$ monolayer ($\kappa$~1.47), at a wavelength of 523nm and a thickness of 0.67nm, a freestanding film has a single-pass absorption of less than 2.3%. Similar values have been reported for graphene and other 2D materials[53, 75]. This presents a great problem for optical absorption devices, where enhancing this number would greatly increase the applications for TMD materials.

This low contrast can make it very difficult to see monolayer materials in optical images. Therefore, contrast enhancement substrates are often utilized to increase the contrast between the monolayer and the substrate[53]. The most typical contrast enhancement substrate used are SiO$_2$/Si substrates; being low-cost and easily accessible, these substrates have been effective in increasing contrast in various monolayers, such as graphene [86] and few-layer TMDs[53]. For instance, if MoS$_2$ is on a 70nm thick SiO$_2$ oxide layer on a Si substrate, over the wavelength range of 450nm to
690nm, the total absorption is over 89% (see Figure 4-1). However, when looking at the exclusive MoS$_2$ absorption, the value is much lower. At a wavelength of 523nm, the MoS$_2$/SiO$_2$/Si system has an absorption of 96.4%, but the MoS$_2$ exclusive absorption is only 20.2%. It is apparent from this that the Si substrate absorbs most of the incident light, while the MoS$_2$ layer absorbs far less. This is not good for light harvesting applications, as the substrate absorbs most of the light.

![Graph showing absorption vs wavelength for MoS$_2$ on a SiO$_2$/Si substrate.](image)

Figure 4-1 MoS$_2$ on a 70nm thick oxide SiO$_2$/Si substrate. Solid line is total absorption and dashed line is MoS$_2$ exclusive absorption. Values calculated by collaborator Haomin Song.

### 4.2 Monolayer Absorption Enhancement in MoS$_2$/Al$_2$O$_3$/Al Nanocavities

In order to increase the exclusive absorption in the MoS$_2$ layer, we replace the SiO$_2$/Si substrates with an Al$_2$O$_3$/Al cavity. Due to the Al reflector having much higher reflection than the Si substrate, the energy absorbed in the system is primarily due to the presence of the monolayer and not the substrate. Therefore, by maximizing the absorption in the cavity, the absorption in the MoS$_2$ layer can be maximized.
To determine the reflection and transmission coefficients of the nanocavity, we calculate the values for each interface, considering the forward and reverse propagating waves for an interface, shown in Figure 4-2. The forward propagating waves, $a_j$, and backward propagating waves, $b_j$, can be easily determined (where $j=1$ is medium 1 and $j=2$ is medium 2):

$$
\begin{bmatrix}
a_1 \\
b_1
\end{bmatrix} = \frac{1}{t_{12}} \begin{bmatrix}
1 & -r_{21} \\
-1 & t_{21} - r_{21} t_{12}
\end{bmatrix} \begin{bmatrix}
a_2 \\
b_2
\end{bmatrix} = M_{1\rightarrow 2} \begin{bmatrix}
a_2 \\
b_2
\end{bmatrix}
$$

where $M_{1\rightarrow 2}$ is the interface matrix, $r_{12}$ and $t_{12}$ are the reflection transmission coefficients from medium 1 to medium 2, and $r_{21}$ and $t_{21}$ are the reflection transmission coefficients from medium 2 to medium 1[49]. Furthermore, the propagation inside a medium can be given by the matrix

$$
N = \begin{bmatrix}
e^{-i\frac{2\pi}{\lambda}nd} & 0 \\
0 & e^{i\frac{2\pi}{\lambda}nd}
\end{bmatrix}
$$

where $d$ is the thickness of the medium and $N$ is the propagation matrix. By coupling the matrices in equation (4.1) and (4.2) in the appropriate order, the system forward and backward propagating waves can be calculated by equation (4.3).
Figure 4-3a plots the results of the MoS$_2$/Si$_2$O$_3$/Al nanocavity system in equation (4.3) as a function of the oxide spacer layer. It can be seen that the optimal range for the oxide thickness is in the 40-50nm range for wavelengths less than 550nm. In this region, the absorption can be over 70%, which is far above the absorption of freestanding MoS$_2$ (~13% including intra-cavity reflection) or MoS$_2$ directly on an Al reflector (~5%). To verify this calculation, the system absorption was calculated using a computer program running a rigorous coupled-wave analysis method (Figure 4-3b)[87]. The results are comparable to the results from equation (4.3) (Figure 4-3a). These results were then compared to the measured values from MoS$_2$/Al$_2$O$_3$/Al cavities with 30, 40, 50, 60 and 70nm oxide films (Figure 4-3c). These samples were fabricated by first depositing an Al layer onto glass substrates via sputtering. The Alumina spacers were then deposited via atomic layer deposition with accurate thickness control. The MoS$_2$ monolayers were fabricated via the CVD process and transferred onto the nanocavity substrates (c.f. section 2.1). The results in Figure 4-3c closely resemble those in Figure 4-3a and 4-3b, indicating a clear increase in the system absorption due to the varying alumina spacer with a maximum at 40nm of oxide thickness. Furthermore, Figure 4-3d demonstrates the exclusive absorption in the MoS$_2$ layer calculated with the rigorous coupled-wave analysis. It can be seen that in the Al$_2$O$_3$/Al cavity, the majority of the absorption is in the MoS$_2$ layer, contrary to the SiO$_2$/Si cavity, where the absorption is primarily at the Si interface (c.f. Figure 4-1).
Figure 4-3 Absorption of MoS$_2$ Monolayers on Al$_2$O$_3$/Al Nanocavities. a) Calculated MoS$_2$/Al$_2$O$_3$/Al cavity with equation (3.3) as a function of the oxide thickness. b) Calculated MoS$_2$/Al$_2$O$_3$/Al cavity via computer simulation of rigorous coupled-wave analysis. c) Measured absorption of MoS$_2$/Al$_2$O$_3$/Al nanocavities. d) Calculated exclusive MoS$_2$ absorption in MoS$_2$/Al$_2$O$_3$/Al cavity via computer simulation of rigorous coupled-wave analysis. Dashed lines line indicates $\lambda=532$nm, the wavelength used in figure 3-4. Computer simulations performed by collaborator Haomin Song.

To further demonstrate the increased light-matter interaction in the MoS$_2$ layer, we analyze the PL signal from the MoS$_2$ monolayers. The relationship between the PL and the pump excitation power is given by $P_{PL} \propto \eta_a \eta_c \eta_q P_{ex}$, where $P_{PL}$ is the PL emission intensity, $P_{ex}$ is the excitation power, and $\eta_a$, $\eta_c$, and $\eta_q$ are the exclusive MoS$_2$ absorption, PL collection efficiency, and quantum efficiency, respectively[88]. Because the carrier lifetimes of MoS$_2$ are dominated by nonradiative recombination[89], the quantum efficiency can be approximated by $\eta_q = \gamma (\gamma + \gamma_{nr})^{-1} \approx \gamma \gamma_{nr}^{-1}$, where $\gamma$ and $\gamma_{nr}$ are the radiative and nonradiative recombination rates. Thus the PL generation, and thus the light-matter interaction, can be enhanced by optimizing equation (4.4):
Thus, by varying the oxide thickness, $\eta_a$ can be modified, altering the PL generation.

Figure 4-4 demonstrates this PL as a function of the oxide thickness. Triangles were pumped with a 532nm laser (5W, Coherent Verdi) focused by a Mitutoyo 50x long working distance objective. The PL was filtered using a 570nm long-pass filter (Chroma 570LP). Shown are the optical micrographs, raster scans, and line plots taken from the line plots from (a) 30nm oxide, (b) 40nm oxide, (c) 50nm oxide, (d) 60nm oxide, and (e) 70nm oxide substrates. Optical micrographs are filtered with a 420nm bandpass filter, and analyzing Figure 4-3, the highest MoS$_2$ exclusive absorption occurs with 30 and 40nm substrates. Looking at the micrographs in Figure 4-4, it is apparent that the 40nm substrate has the highest contrast, demonstrating that the absorption is mostly in the MoS$_2$ layer. Furthermore, as can be seen from the PL spectra taken in Figure 4-4f, the triangle at 60nm generated the most PL. This is in contrast to what was predicted in Figure 4-3d, where the optimal oxide thickness is between 40 and 50nm. Note that there is some fluctuation in the PL spectrum in Figure 4-4f. To verify that these fluctuations in the PL spectra in Figure 4-4f are from the optics used in the experiment, a separate spectrum was taken using a Renshaw inVia microscope (Figure 4-4g), indicating that the spectral fluctuations in Figure 4-4a though 4-4f are not due to the cavity or MoS$_2$ sample. In order to account for the shift between the absorption and emission peak, one must closely inspect equation (4.4). $\eta_a$ has been demonstrated to be dependent on the oxide thickness, and $\gamma_m$ is independent of the substrate. Therefore, both $\gamma$ and $\eta_c$ must be further evaluated to find dependence on oxide thickness.
Figure 4.4 PL characterization of MoS$_2$ monolayers on different nanocavities. Optical micrographs, PL raster scans, and PL line plots of MoS$_2$ triangles on nanocavities with (a) 30nm thick Al$_2$O$_3$ spacer layer, (b) 40nm thick Al$_2$O$_3$, (c) 50nm thick Al$_2$O$_3$, (d) 60nm thick Al$_2$O$_3$, and (e) 70nm thick Al$_2$O$_3$. Dashed horizontal lines in the PL raster scan indicate data taken for the PL line plots. f) PL spectra taken from MoS$_2$ monolayers on Al$_2$O$_3$/Al nanocavities. g) PL spectra taken using a Renishaw inVivo PL microscope from a 40nm Al$_2$O$_3$ thick sample.

Figure 4.5 demonstrates the simulated radiation pattern of the MoS$_2$ monolayer on a nanocavity substrate at the wavelengths of (a) 650nm, (b) 685 nm, and (c) 720nm (values taken from the short wavelength end of the PL spectrum, PL maxima, and the long wavelength end of the PL spectrum).
spectrum, c.f. Figure 4-4g). The pattern is normalized to the maximum of each wavelength. The grey region indicates the angular region that is not collected by the lens (NA=0.55). It can be determined that the emission pattern is largely wavelength independent, as well as spacer thickness independent; however the magnitude of the emission intensity varies, indicating an effect of the oxide thickness on the magnitude of the output intensity. Therefore, it can be safely assumed that the shift between the absorption and emission peak is not due to $\eta_c$ varying caused by the change of oxide thickness. Therefore, the reason for the shift between Figure 4-3 and Figure 4-4 is due to a change in emission rate as a function of the oxide thickness.

Figure 4-5 Simulated spacer-thickness dependent radiation pattern of the MoS$_2$ monolayer on a nanocavity at three different wavelengths of (a) 650 nm, (b) 685 nm and (c) 720 nm, respectively. Light in the grey angular regions cannot be collected due to the NA (0.55) of the collection lens. Calculations performed by collaborator Haomin Song.
4.3 Modification of PL Emission Rate in MoS₂/Al₂O₃/Al Nanocavities

It has long been demonstrated that the spontaneous emission rate of a dipole within a nanocavity can be modified due to the presence of its own field[90]. Using a classical model, the emission rate from a dipole can be calculated by using the equation[90]

\[ \gamma = \gamma_o \left( 1 + \frac{6\pi e_o}{P_o k^3} \text{Im}[E_{0e}'] \right) \]  \hspace{1cm} (3.6)

where \( \gamma_o \) is the emission rate without the presence of the cavity, \( e_o \) is the vacuum permittivity, \( P_o \) is the dipole moment, \( k \) is the wavenumber, \( \text{Im}[\cdot] \) represents the imaginary component, and \( E_{0e}' \) is the modification of the electric field at the dipole due to the presence of the cavity. In order to calculate the modification of the electric field, we developed a method to calculate the Hertz potential \( \Pi \), from which the electric field distribution can be calculated \( \vec{B} = \nabla \times \vec{A}, \vec{E} = -\nabla \phi; \vec{A} = v^{-2} \partial \vec{\Pi} / \partial t, \phi = -\nabla \cdot \vec{\Pi} \)[49]. In order to do this, the boundary conditions must be met. This requires that \( e \Pi_z, e \Pi_x, e \partial \Pi_z / \partial z, \) and \( e \partial \Pi_z / \partial z + e \partial \Pi_x / \partial z \) must be continuous. \( e \) is the permittivity of the medium. Because the orientation of the dipole changes the effect on the Hertz potential, we consider two cases: a dipole orthogonal to the interface \( \left( \Pi = \hat{z} \Pi_z \right) \) and parallel to the interface \( \left( \Pi = \hat{x} \Pi_x + \hat{z} \Pi_z \right) \). To simplify this calculation, a matrix method was derived to calculate the Hertz potential for both perpendicular and parallel dipoles, allowing the modification of the field to be calculated.

For a dipole oriented orthogonal to an interface \( \left( \Pi = \hat{z} \Pi_z \right) \), the boundary conditions can be satisfied by the following matrix equation (4.7):

\[
\begin{bmatrix}
\Pi_{2}^+ \\
\Pi_{2}^-
\end{bmatrix} = \frac{n_2}{n_1} \begin{bmatrix}
1 & r_{12}^\parallel \\
r_{12}^\parallel & 1
\end{bmatrix} \begin{bmatrix}
\Pi_{1}^+ \\
\Pi_{1}^-
\end{bmatrix} = I_{1 \rightarrow 2} \begin{bmatrix}
\Pi_{1}^+ \\
\Pi_{1}^-
\end{bmatrix}
\]  \hspace{1cm} (4.7)

where \( \Pi^+ \) and \( \Pi^- \) represent the Hertz potential component propagating in the positive and negative direction respectively, \( t^\parallel \) and \( r^\parallel \) are the p-polarized transmission and reflection Fresnel coefficients[49]. Subscripts represent the medium under consideration. The propagation matrix can be calculated by the propagation matrix, \( P \),
where $k_z$ is the z-component of the wave vector in the medium and $d$ is the distance travelled in the z direction. The Hertz potential across the dipole itself must also be accounted for due to the presence of the dipole itself:

$$\begin{bmatrix} \Pi_{z=0+}^+ \\ \Pi_{z=0+}^- \end{bmatrix} = \begin{bmatrix} e^{ik_z d} \\ e^{-ik_z d} \end{bmatrix} \begin{bmatrix} \Pi_{z=0}^+ \\ \Pi_{z=0}^- \end{bmatrix} = p \begin{bmatrix} \Pi_{z=0}^+ \\ \Pi_{z=0}^- \end{bmatrix} \tag{4.8}$$

where $0^+$ and $0^-$ denote the limit approaching the dipole ($z=0$) from the positive z and negative z directions, respectively, and $p_o$ is the dipole moment.

The dipole is modeled to be perpendicular to the interface, lying directly atop the MoS$_2$ layer above the Al$_2$O$_3$ oxide and Al reflector. Concatenating each interface and propagation matrix from equations (4.7) and (4.8) respectively, the Hertz potential can be solved by equation (4.10):

$$\begin{bmatrix} \Pi_{z=0+}^+ \\ \Pi_{z=0+}^- \end{bmatrix} = \begin{bmatrix} \Pi_{z=0}^+ \\ \Pi_{z=0}^- \end{bmatrix} + \begin{bmatrix} i \frac{p_o}{2 \varepsilon k_z} \\ -i \frac{p_o}{2 \varepsilon k_z} \end{bmatrix} \tag{4.9}$$

where $\Pi_{z=0+} = (\Pi_{z=0}^+ + \Pi_{z=0}^-)$.

The interface, propagation, and dipole matrices can be calculated as below, similar to the orthogonal case:

$$\begin{bmatrix} \Pi_{z=d}^+ \\ \Pi_{z=d}^- \end{bmatrix} = \begin{bmatrix} e^{ik_z d} \\ e^{-ik_z d} \end{bmatrix} \begin{bmatrix} \Pi_{z=0}^+ \\ \Pi_{z=0}^- \end{bmatrix} = p \begin{bmatrix} \Pi_{z=0}^+ \\ \Pi_{z=0}^- \end{bmatrix} \tag{4.8}$$

where $\Pi_{z=d} = (\Pi_{z=d}^+ + \Pi_{z=d}^-)$.
\[
\begin{bmatrix}
\Pi_{z2+} \\
\Pi_{z2-} \\
\frac{k_x}{k_o} \Pi_{x2+} \\
\frac{k_x}{k_o} \Pi_{x2-}
\end{bmatrix} = \begin{bmatrix}
\frac{n_2}{n_1} & \frac{n_2}{n_1} t_{12} & \frac{1}{2k_{z1}} \left(1 - \frac{\epsilon_2}{\epsilon_1}\right) & \frac{1}{2k_{z1}} \left(1 - \frac{\epsilon_2}{\epsilon_1}\right) \\
\frac{n_2}{n_1} t_{12} & \frac{n_2}{n_1} & \frac{1}{2k_{z1}} \left(1 - \frac{\epsilon_2}{\epsilon_1}\right) & \frac{1}{2k_{z1}} \left(1 - \frac{\epsilon_2}{\epsilon_1}\right) \\
0 & 0 & \frac{n_2}{n_1} & \frac{n_2}{n_1} \\
0 & 0 & \frac{n_2}{n_1} t_{12} & \frac{n_2}{n_1} t_{12}
\end{bmatrix}
\begin{bmatrix}
\Pi_{z1+} \\
\Pi_{z1-} \\
\frac{k_x}{k_o} \Pi_{x1+} \\
\frac{k_x}{k_o} \Pi_{x1-}
\end{bmatrix}
\]

(4.12)

\[
\begin{bmatrix}
\Pi_{z+d} \\
\Pi_{z-d} \\
\frac{k_x}{k_o} \Pi_{x+d} \\
\frac{k_x}{k_o} \Pi_{x-d}
\end{bmatrix} = e^{ik_z d} \begin{bmatrix}
e^{ik_z d} & 0 & 0 & 0 \\
0 & e^{-ik_z d} & 0 & 0 \\
0 & 0 & e^{ik_z d} & 0 \\
0 & 0 & 0 & e^{-ik_z d}
\end{bmatrix} \begin{bmatrix}
\Pi_{z+} |_{z=0} \\
\Pi_{z-} |_{z=0} \\
\frac{k_x}{k_o} \Pi_{x+} |_{z=0} \\
\frac{k_x}{k_o} \Pi_{x-} |_{z=0}
\end{bmatrix} = P \begin{bmatrix}
\Pi_{z+} |_{z=0} \\
\Pi_{z-} |_{z=0} \\
\frac{k_x}{k_o} \Pi_{x+} |_{z=0} \\
\frac{k_x}{k_o} \Pi_{x-} |_{z=0}
\end{bmatrix}
\]

(4.13)

\[
\begin{bmatrix}
\Pi_{z+} |_{z=0^+} \\
\Pi_{z-} |_{z=0^+} \\
\frac{k_x}{k_o} \Pi_{x+} |_{z=0^+} \\
\frac{k_x}{k_o} \Pi_{x-} |_{z=0^+}
\end{bmatrix} = \begin{bmatrix}
0 \\
0 \\
\frac{k_x}{k_o} i p_0 \\
\frac{k_x}{k_o} i p_0
\end{bmatrix}
\]

(4.14)

The Hertz potential can be once again calculated as...
For an isotropically oriented dipole, the emission rate can be calculated from its perpendicular and parallel components, \( \gamma = \gamma^+ / 3 + 2 \gamma^3 / 3 \). However, due to the presence of the cavity, the emission of the parallel dipole contributes dominantly to the signal collected. This can be seen in Figure 4-6, where the far-field spectrum of the MoS\(_2\) dipole emission is plotted. The parallel dipole is plotted in Figure (4-6a) and an orthogonal dipole is considered in Figure 4-6b (note the difference in scale bars is two orders of magnitude). Blue lines represent the lens collection range. It is clear that the parallel dipole signal is much larger than the perpendicular dipole in this lens range, due to the cavity total internal reflection containing the perpendicular dipole field, and propagating plasmonic waves along the Al surface. Therefore, when calculating the dipole emission rate modification, only the parallel component is used for the nanocavity substrates and not the isotropic emission rate.

\[
I_{\text{air} \rightarrow \text{MoS}_2} P_{\text{MoS}_2} I_{\text{MoS}_2 \rightarrow \text{Al}_2\text{O}_3} P_{\text{Al}_2\text{O}_3} I_{\text{Al}_2\text{O}_3 \rightarrow \text{air}}
\]

\[
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}
\]

\[
= \begin{bmatrix}
\Pi_{z^+|\text{Al}} \\
\Pi_{z^-|\text{air}} \\
\frac{k_x}{k_o} \Pi_{x^+|\text{Al}} \\
\frac{k_x}{k_o} \Pi_{x^-|\text{air}}
\end{bmatrix}
\]

\[
= \begin{bmatrix}
0 \\
0 \\
\frac{k_x}{k_o} \frac{ip_0}{2k_x c_{\text{air}}} \\
-\frac{k_x}{k_o} \frac{ip_0}{2k_x c_{\text{air}}}
\end{bmatrix}
\]

and the electric field at the dipole’s location can be calculated by

\[
P_{x}^{\text{eff}} = \frac{k^3}{2\pi} \int_{0}^{1} \left[ \frac{1}{2} \Pi_{x^-|\text{air}} u^3 + \Pi_{z^-|\text{air}}(u - u^3) \right] du
\]
The relative emission rate, $\gamma_{eff} = \gamma/\gamma_0$, is plotted in Figure 4-7 (red dots). Also plotted are the exclusive MoS$_2$ absorption (blue dots) and the measured PL values (green bars). The black curve is the normalized total PL enhancement in equation (4.4). It can be noted that the normalized PL intensity resembles the measured PL values much better than the exclusive absorption. This effectively demonstrates that both the PL absorption and the emission rate must be included to effectively model the PL emission power.
Figure 4-7 Nanocavity Enhancement on MoS$_2$ PL Generation. Red dotted line is the effective emission rate. Blue dotted line is the exclusive absorption of the MoS$_2$ layer from Figure 4-3d. Black curve is the normalized PL intensity including both the absorption and emission enhancement. Green bars are the range of the PL values from Figure 4-4.

In order to determine the effectiveness of PL generation for the Al$_2$O$_3$/Al nanocavity, we compare it against the common SiO$_2$/Si contrast enhancement substrates. Due to the reduced exclusive MoS$_2$ absorption, the SiO$_2$/Si cavity has a much lower PL generation efficiency. Figure 4-8 plots the total PL enhancement for both substrates. The Al$_2$O$_3$/Al nanocavity (black curve) has a maximum over 2.5 times larger than the SiO$_2$/Si maximum, which has its maximum at a much thicker oxide substrate. This effectively demonstrates that the nanocavity substrate not only increases the absorption (20.2% for SiO$_2$/Si substrate, 37% for Al$_2$O$_3$/Al at 532nm), but also the PL emission power of the MoS$_2$ monolayer.
In summary, with the addition of a simple nanocavity structure, a method was developed to both enhance the absorption and modify emission rate of a MoS\(_2\) monolayer. Using a simple MoS\(_2\)/Al\(_2\)O\(_3\)/Al nanocavity with only tens of nanometers of oxide spacer, the exclusive absorption can be increased to over 70\%, much more than a free-standing monolayer or a SiO\(_2\)/Si contrast enhancement substrate. Not only does this make the nanocavity structure an excellent contrast enhancement substrate, but an excellent substrate for optical absorption based devices, such as phototransistors[91] or solar harvesters[92]. By tuning the oxide layer, the absorption maximum can be tuned for different wavelengths in the MoS\(_2\) absorption spectrum, making it a flexible design for device engineering. Furthermore, the emission rate can also be tuned by varying the oxide thickness, giving further design flexibility. Overall, the nanocavity described in this chapter is an enhancement substrate that, using a simple, easy to fabricate design, provides excellent contrast imaging, absorption enhancement, and emission rate tunability.
Chapter 5

Particle Characterization Using Ultra-High-Q Microresonators

In Chapter 4, we discussed the enhancement of optical absorption and emission in 2D material using nanocavities. These Al₂O₃/Al cavities were simple to fabricate and resulted in enhanced light-matter interaction in a very small planar cavity. Although this method led to absorption and PL enhancement over traditional substrates, the ultimate Quality-factor (Q-factor) of the nanocavity is low. In order to create much larger enhanced light-matter interaction in a high-Q Factor cavity, ultra-high-Q microresonators provide an excellent platform to enable strong light-matter interactions and ultra-high field enhancement. It is through these ultra-high-Q cavities, and with 2D material integration, that can provide new opportunities for the next generation optical devices. This chapter discusses a method to demonstrate the enhanced light-matter interaction within ultra-high-Q microresonators, and the current steps taken to integrate 2D materials into microresonator systems are discussed in the next chapter.

Whispering Gallery Mode (WGM) Microresonators, such as microspheres, microdisks, and microtorroids, have garnered much attention in the optical community as devices with ultra-high-Q factors, achieving values as high as 10⁹[35]. These resonators have been an expanding platform for many optical devices, including lasers[93], frequency combs[94], and in particular, particle sensing[36, 37]. Nanoparticle detection remains a difficult problem in sensing, and microresonator based devices have demonstrated the capability to detect particles as small as 30nm in diameter[95]. Several methods based on mode splitting[37] and mode-shifting[95] have been utilized to make microresonator based devices an excellent platform in nanoparticle detection. As a particle enters the field in the microresonator, its refractive index is larger than that of the air surrounding the cavity,
causing the optical-path-length of the cavity to change. This leads to a shift in the mode’s resonant frequency, which can be detected using a scanning laser. Furthermore, the particle induces two standing waves that have slightly different resonant frequencies (based on the node and anti-node), allowing for another method to detect the particle size by the difference between the mode and the new split mode. Because of the resonator’s large Q factor, these mode shifts have very high resolution, leading to particles with very small diameters to be accurately detected[96].

However, although this particle detection is very sensitive, because it is based on the particle’s refractive index, it lacks the ability to characterize the particle landing on the resonator. In order to mitigate this problem, in this chapter we discuss a method to enhance the particle detection capabilities of microresonators using Raman spectroscopy[97]. A review of ultra-high-Q factor microresonators is briefly discussed before describing a system using Raman spectroscopy to enhance microsphere resonators as a platform to both detect and characterize particles[39]. Furthermore, by using the large build-up factor within the microresonator cavity, the microsphere itself can enhance the Raman signal generated by the adhered particle[98].

5.1 Ultra-High-Q Whispering Gallery Mode Microresonators

Ultra-high-Q WGM resonators utilize continuous total internal reflection to confine photons in a cavity. Commonly used microresonator devices are the microtorroid (microdisk with reflowed edges, Figure 5-1a) and microsphere resonators (fig. 5-1b). These devices have a smooth surface, achieving very low scattering loss[35]. This causes very little loss in the device, as well as a very large field build-up within the cavity. Furthermore, as the mode that propagates along the surface of the resonator evanescently leaks out into the surrounding medium, it is susceptible to perturbations in the environment. This allows materials adhered to the surface, such as microparticles or 2D materials, to interact with the optical mode without incurring large losses. As discussed in chapter 4,
the light matter-interaction with TMD monolayers can be increased dramatically through the use of resonant cavities. Therefore, by utilizing the ultra-high-Q resonators, this light-matter interaction can be increased to an extraordinary level. However, this work is still in progress, as the 2D-microresonator devices are still in development (Figure 5-1c). This will be further discussed in chapter 6. The remaining portion of this chapter will discuss how microresonators enhance light-matter interaction in microparticle sensing, paving the way for these 2D-microresonator devices to be realized.

Figure 5-1 Microresonator Devices. a) SEM image of a microtorroid resonator. b) Microsphere resonator with adhered particle coupled with a tapered silica fiber. c) Photoluminescence image of a microsphere resonator with grown WS$_2$ monolayers.

When a particle enters the evanescent field of a WGM mode, the optical path length in the device changes due to the increased refractive index in the mode[95]. This causes the mode to shift in frequency, which can be detected, allowing the microresonator to be used as a particle sensor via mode shifting. A secondary method of particle detection occurs when the particle scatters light in the resonator, generating two standing waves with one where the particle is located at the node and the other where the particle is at the anti-node[45]. These waves experience different frequency shifts, and thus there is a mode splitting in the transmission spectrum when the particle is adhered. Although these two methods have highly accurate particle detection capabilities, they lack the ability
to characterize the particle. This is why utilizing the scattered Raman signal from the particle allows for both particle detection and characterization.

In this work, microsphere resonators are used as resonant devices to detect and characterize particles. The steps in fabricating these devices are shown in Figure 5-2. First, an optical fiber (Corning SM600) is tapered using a hydrogen torch while the ends are pulled using computer controlled actuators (Figure 5-2a)[99]. By monitoring the transmission of the fiber, one can monitor the thickness of the tapered fiber. When the taper is still large, the transmission of the fiber remains single mode, and has a flat transmission intensity. As the fiber thins, the fiber turns into a multimode fiber with the surrounding air serving as the cladding, generating an oscillating transmission pattern. When the thickness of the fiber approaches the wavelength of the light propagating through the fiber (~760nm in this case), the transmission becomes single mode again (Figure 5-2b). Using this process, the transmission of the fiber can remain at over 95% while exposing the evanescent field of the optical wave. This makes fiber tapers excellent in coupling light into microsphere resonators, as well as a fundamental stage in the fabrication of the microsphere itself. To fabricate the microresonator, the fiber taper is broken and one end is mounted in a rotational stage. The fiber is then exposed to a CO\textsubscript{2} laser beam, of which the silica fiber is highly absorptive (Figure 5-2c). This causes the thin fiber to melt, and surface tension pulls the melted glass back along the fiber taper, forming a microsphere. By rotating the taper during this process causes the microsphere to grow in size and be centered on the fiber taper stem (figure 5-2d). By centering a very thin stem on the sphere, it causes sufficient distance between the sphere’s equator and the stem, preventing the mode from losing energy into the stem. Spheres were fabricated with diameters between 15-250\textmu m. The smaller spheres contained fewer modes propagating through the device, while the larger spheres have higher quality modes due to a more ideal spherical shape (stem is smaller in comparison to the sphere). Therefore, spheres used in this experiment have a diameter between 40-70\textmu m, generating modes with sufficient mode separation but quality factors above $10^7$-$10^8$. 
Figure 5-2 Microsphere Resonator and Fiber Taper Fabrication. a) Single mode fiber is slowly softened with a hydrogen torch. b) Fiber is slowly pulled until the diameter is below 1μm. Optical image has a 10μm standard sphere to demonstrate fiber diameter. c) Fiber taper is broken and slowly melted with CO$_2$ laser. d) Microsphere is formed by further heating the taper and increasing CO$_2$ laser intensity. Surface tension forms sphere as the glass is melted and rotating the fiber helps center the stem on the sphere.
5.2 Raman Spectroscopy

Raman spectroscopy had been demonstrated as an effective tool for material characterization since its discovery in 1928, for which C. V. Raman won the Nobel Prize in Physics in 1930[97]. It has application in a wide variety of sciences, from material thermal detection[100], molecule characterization[101], and most recently, characterization of layer numbers in 2D and layered materials[23], as mentioned in section 2.1. Through its ability to detect molecules through their vibrational spectra, Raman spectroscopy can provide a unique label-free approach to characterize materials[99].

As shown in Figure 5-3a, when a photon is incident on a molecule, it has a small probability to undergo inelastic scattering to yield a photon of slightly less energy, with the remaining energy manifesting as vibration of the molecule. Due to this loss of energy, the frequency of the photon emitted is reduced, and this redshift can be detected with a spectrometer. This process of energy reduction is known as the Stokes shift. An Anti-Stokes shift can also be generated when the molecule, with an already stimulated vibration mode, produces a photon of slightly higher energy. Due to the increased probability of the Stokes shift when measuring spontaneous Raman signals, the work here is focused on detecting this shift. The Raman spectrum for a polystyrene (PS) microparticle is seen in Figure 5-3b (taken from reference[102]). It can be easily seen that the vibrational modes of the material are strong with vibrations at 1000 cm\(^{-1}\), 2850 cm\(^{-1}\), 2905 cm\(^{-1}\), and 3050 cm\(^{-1}\). Of particular interest to this work are the higher shift energy modes (2850 cm\(^{-1}\), 2905 cm\(^{-1}\), and 3050 cm\(^{-1}\)) which are present due to the characteristic C-H bond in polystyrene.
Figure 5-3 Raman Spectroscopy. a) Diagram of Raman scattering energy levels. Green: incident photon and energy level. Red: Stokes emitted photon and energy level. Blue: Anti-stokes emitted photon and energy level. b) Raman spectrum of a polystyrene microparticle taken from reference [102]. Labeled are the characteristic vibrational modes for the molecule. c) Raman spectrum taken from monolayer WS$_2$.

Because the emitted photon is dependent on the composition of the molecule probed, each type of molecule produces a different Raman spectrum. This makes Raman spectroscopy ideal for identifying particles of unknown chemical compositions. One such example is described in chapter 2, where Raman spectroscopy is mentioned as an ideal method to determine the difference in layer number for 2D and layered materials (Figure 5-3c)[23]. The bonds in the layered crystal change and this affects its Raman spectrum, allowing the number of layers in the material to be determined.

Due to its label free property, Raman response has been widely utilized in many scientific fields. However, the Raman response of many particles is incredibly weak, with a scattering cross-
section as low as $10^{-30}$ cm$^2$ per molecule per steradian [103]. Many techniques have been developed to enhance the Raman signal generated from molecules, including Surface Enhanced Raman Scattering (SERS)[104], resonance Raman Spectroscopy[105], and Coherent Anti-Stokes Raman Spectroscopy (CARS)[102, 106]. Although these methods provide an excellent manner to characterize particles, they lack the inherent particle detection sensitivity that microresonator devices can provide. To this end, for the rest of the chapter, we discuss the enhancement of microresonator particle detection, which can provide both particle characterization and detection capabilities when coupled with Raman spectroscopy.

### 5.3 Microresonator Based Raman Spectroscopy

In order to measure the Raman signal from adhered particles, the Micro-Raman microscope in Figure 5-4 was constructed. First, the output from a tunable exterior cavity laser diode (ThorLabs, TLK-L780M, $\lambda=750$ - 780nm, output power < 60mW) passed through a Faraday isolator and was coupled into a single mode fiber (Corning SM600) using a 40x objective lens. The fiber was then sent through a paddle waveplate (ThorLabs, FPC560) so that the polarization of the light could be controlled to ensure maximum coupling into a TE or TM mode of the microsphere resonator. This fiber was then tapered using the method illustrated in Figure 5-2, and transferred into the Micro-Raman microscope (Figure 5-4). The remaining end of the fiber was inserted into a photodiode (ThorLabs, PDA36A) so that the fiber transmission could be monitored. The scattered signal from the particle was collected by a long working-distance objective lens (50x Mitutoyo, NA=.55). The collected scattering is split using a dichroic mirror (785nm) with the transmitted signal detected by a CCD camera so that the particle can be located at the focal point of the lens. The reflected signal is filtered using an 810nm long-pass filter before the signal is detected using a spectrometer (PI Acton 2500i with a liquid nitrogen cooled CCD camera).
Figure 5-4 Micro-Resonator Raman Microscope Pumped via Fiber Taper. The output from an external cavity tunable diode laser is coupled into SM600 optical fiber before going through a paddle waveplate. The fiber is tapered for a short region and the output is detected by a photodiode. In the tapered region, the fiber is critically coupled with the microsphere resonator (MS). The scattered signal is collected by a 50x Long-Working Distance Objective (LWDO). The signal is split by a 785nm Dichroic Mirror (DM). Transmitted signal is focused onto a CCD detector and reflected signal is filtered using an 810nm Long-pass filter (LFP) before detected by a spectrometer.

To demonstrate the capabilities of microsphere resonator Raman microscopy, we measured the Raman spectrum from adhered 2μm polystyrene microparticles (Duke Scientific, Diameter of 2.04μm ± 0.045μm). To adhere these particles, a silica probe was formed using a plasma fusion splicer (Ericsson FSU-975). The probe is then coated with the PS particles and delivered to the microsphere (Figure 5-5a). The probe is then carefully brought close to the microresonator using both manual and piezo-controlled actuators. Carefully, the probe is brushed against the resonator, depositing the particle. The particle should be located at the equator of the microsphere in order to expose it to the higher Q-factor resonant modes in that region. Furthermore, the particle is located on the back- or right-side of the sphere when looking from the top, as any light scattered by fiber taper defects will be reflected on the left and bottom of the sphere, generating more background signal. To
verify that a single particle is properly deposited along a clean region of the microsphere, both top and side CCD cameras are checked.

Figure 5-5 Polystyrene Particle Deposition. a) Particle deposition process with images from both the side and top of the resonator. b) Microresonator mode before particle deposition. c) Resonator mode after the particle is deposited.

Figure 5-5b shows the mode from the microsphere resonator before the particle is adhered to the surface. The original Q factor \((Q = \nu/\Delta \nu)\) is \(2.4 \times 10^7\). After the particle is deposited, the Q factor reduces dramatically due to scattering loss (mode shown in Figure 5-5c). The Q factor after
deposition is $3.2 \times 10^6$. Although the particle is large, this effectively demonstrates that the resonator can detect the presence of an adhered particle through the changes in resonant modes.

Upon verification of particle location, the Raman spectrum from the particle can then be collected. Figure 5-6a shows a typical Raman spectrum taken from a 2μm PS particle, with an integration time of 30s. The pump laser is locked to the resonant frequency of the mode using our frequency locking system described in the Appendix. The incident power is 4.5mW before coupling into the fiber, with estimated losses of 40% due to coupling (~1.8mW before the resonator). The left most peak in the figure is the laser breakthrough from the 810nm long pass filter. The peaks between 810nm and 950nm are the silica Raman spectrum, generated as the wave propagates in the microsphere itself, producing a strong Raman signal. This is inherent in any optical-fiber-based Raman spectroscopy, as silica itself will generate a broadband Raman signal up to 40 THz in Raman shift[107]. Between 970nm and 1000nm, three PS Raman peaks can be seen (2850 cm$^{-1}$, 2905 cm$^{-1}$, and 3050 cm$^{-1}$ peaks, respectively). This effectively demonstrates that Raman spectroscopy can enhance the detection capabilities of microresonator based particle sensors by providing particle detection and characterization capabilities.

Figure 5-6 Microresonator Enhanced Polystyrene Raman Spectrum. a) Raman spectrum taken from a 2μm PS particle adhered to a 50μm microsphere resonator. Black line represents the 810 filter line. b) Raman spectra plotted in (a) focusing on the PS Raman peaks.
5.4 Raman Scattering Enhancement Using Microresonators

In section 5.3, Raman spectroscopy was utilized to enhance the particle detection capabilities of microresonators. On the other hand, microresonators also enhance the Raman scattering from the adhered particle, making this a symbiotic relationship between the resonator and Raman spectroscopy. Because the Raman scattering intensity is linearly dependent on the incident pump intensity, it is very weak due to the small molecular Raman cross section and it can be a challenge to detect Raman signals from particles. However, with the built up field within the resonator, microresonators can enhance the field exposed to the particles, generating more Raman scattering. Equation (5.1) calculates, B, the build-up factor (field enhancement) for a critically coupled WGM microresonator:

$$ B \approx \frac{Q_{ex} \lambda}{4 \pi^2 n R} $$  \hspace{1cm} (5.1)

where $Q_{ex}$ is the extrinsic Q-factor of the resonator, $\lambda$ is the resonant wavelength, n is the refractive index, and R is the radius of the microresonator. For Resonators used in these experiments, ($Q_{ex} \sim 10^8$, $\lambda \sim 760$nm, $R \sim 25$μm) the build-up field enhancement is approximately $B \sim 5 \times 10^5$. This is a very large field enhancement, providing orders of magnitude larger pump fields to the particle. This in turn generates orders of magnitude larger amounts of Raman scattering, making it easier to detect the Raman spectrum.
In order to demonstrate this, we compare the Raman signals generated using microresonator enhanced Raman spectroscopy to those of particles adhered directly to the fiber-taper[99]. The blue curve in Figure 5-7 shows the Raman spectra collected from a 2\(\mu\)m PS particle adhered directly to a microresonator. The incident power is 4.5mW with estimated losses of 40% (~1.8mW before the resonator) and the signal was captured using a 2s integration time. The red curve plots the Raman signal collected from the same particle adhered directly to the fiber taper under the same pump conditions but for an integration time of 30s. When comparing the signal level to the background, the particle on the resonator has more than three times the signal as the particle on the fiber taper for an integration time that is fifteen times shorter. This effectively demonstrates that, for the same particle with the same incident conditions, resonator enhanced Raman spectroscopy is superior to that of particles directly adhered to the fiber taper.
In this chapter, microsphere resonators were demonstrated to have enhanced characterization and detection capabilities for microparticles. Through the characterization capabilities of Raman scattering spectroscopy, microresonators were shown not only to detect microparticles adhered to their surface, but to also label-free characterize the particles through their Raman spectrums. A 2μm polystyrene particle was characterized, demonstrating that the Raman spectrum could be obtained from a microsphere resonator. Also, through the internally built-up field, the microresonator itself enhances the intensity of the Raman scattering of the particle, making microresonators an excellent platform to enhance Raman scattering. Although several techniques have been developed to enhance the Raman scattering of particles in microresonators, these methods compromise the particle detection capabilities of the resonator [108]. This makes microresonator enhanced Raman spectroscopy ideal when it is required to both characterize and detect microparticles.
Chapter 6
Future Work

The work presented in this dissertation has been focused on the characterization and enhancement of 2D materials and optical resonators including both of the planar and microsphere geometry. Chapter 2 utilizes the unique properties of 2D materials in second harmonic generation, and it was discovered that mono- and few-layer TMD materials are excellent materials for SHG generation. However, their properties vary widely depending on the number of layers of material present due to varying crystal symmetry in the layers. By characterizing the material, it was determined that the second order nonlinear susceptibility of the material is on the order of nm/V, over three orders of magnitude larger than typical nonlinear materials. Furthermore, by calculating the band structure with DFT calculations, it was revealed that the extraordinarily large susceptibility value was due to resonance in the band structure and an increased JDOS in monolayer WS₂. This was then taken a step further in chapter 3, where by doping a TMD alloy, the band structure was modified, allowing the nonlinear properties to be engineered. This demonstrates that by tuning the doping concentration level in 2D materials, the nonlinear susceptibility spectrum can be modified.

Due to this discovery that TMD monolayers have extraordinary nonlinear generation, they would make excellent materials to enhance existing nonlinear devices that lack second-order nonlinearities due to crystal symmetry. Systems based on silica fiber have difficulty generating second-order nonlinearity because of their amorphous structure, and thus are limited to surface nonlinear generation[47]. By adding 2D materials to silicon and silica devices, they can enhance the original system without dramatically increasing loss from scattering or absorption due to their atomic thickness. This has been demonstrated with graphene, where biasing the graphene layer leads to
varying levels of absorption and can be used as optical modulators[21]. Similarly, 2D materials can add increased nonlinearity to optical systems. By using evanescent coupling in silica tapers or D-shaped polished fiber, 2D TMD layers could be implemented to impart second-order nonlinearities without inducing loss in optical fibers. Similarly, they can be fabricated directly atop on-chip waveguides, an even simpler method to integrate nonlinearity into centrosymmetric material systems. Furthermore, by engineering the nonlinear response for these materials, they have the ability to be easily tuned to enhance/suppress at specific operating wavelengths, something that can be difficult to achieve in optical fiber systems.

Although the atomic thickness played an important role in the nonlinear generation discussed in chapters 2 and 3, the atomic thickness of the material was exposed to be a hindrance for absorption and light emission devices in chapter 4. The inherent atomic thickness leads to very low absorption, and thus monolayer materials need to be enhanced by their substrates to make them suitable for optical devices. A simple method for this was provided in chapter 4, where using a planar MoS$_2$/Al$_2$O$_3$/Al cavity, the MoS$_2$ absorption was increased to over 70% by tuning the oxide spacer thickness. This simple cavity leads to increased light-matter interaction and causes the light to be absorbed primarily at the monolayer region instead of other cavity interfaces, resulting in a device that greatly enhances the monolayer MoS$_2$’s absorption. Furthermore, by tuning the oxide thickness, the device also modifies the PL emission of the monolayer, allowing for further design freedom in light emission based devices. Although this simple cavity structure was demonstrated to be an efficient enhancement mechanism for enhancing the light-matter interaction with 2D layers, the overall energy storage in the device was weak. In order to improve this low-Q cavity, higher-Q cavities should be utilized to further improve the light-matter interaction. One such family of ultrahigh-Q optical resonators are the family of whispering gallery mode optical microresonators, such as microspheres. In chapter 5, we discussed the ability for microresonators to detect and characterize particles using Raman spectroscopy. Raman spectra were taken from microparticles, demonstrating
that it is an effective mechanism for particle characterization and detection. Furthermore, the Raman spectra were enhanced by the built-up field within the resonator, demonstrating that microresonator based Raman spectroscopy not only enhances the characterization ability of microresonators, but enhances the Raman scattering of the adhered particle.

In order to further enhance the optical performance of monolayer materials work done in chapter 4, I propose implementing the microresonator system in chapter 5 to enhance the resonator capabilities. By replacing the planar nanocavity with a microresonator, the field interacting with the monolayer material is much larger, generating new possibilities for absorption, PL emission, and nonlinear generation. In chapter 5, it was demonstrated that by placing a microparticle on the surface of the resonator, the Q-factor of the resonator is reduced because the particle scatters light out of the cavity. However, due to the atomic thickness of 2D materials, this scattering loss can be minimized; this allows one to effectively ‘dress’ the microresonator in 2D materials, imbuing their optical characteristics to the microresonator device without introducing significant scattering loss. Microresonator devices have been demonstrated very recently, but these devices are based on fabricating microresonators around the 2D TMD material, greatly reducing their overall device quality and manufacturing capability[38]. By fabricating a microdisk resonator around the 2D material (because the 2D material is much more difficult to fabricate), it prevents the surface of the disk from being reflowed into a higher-Q microtorroid cavity, reducing device quality. Therefore, the device I propose utilized the opposite approach: fabricating the microresonator and then ‘dressing’ it with the 2D material rather than fabricating the resonator below the material. Preliminary work on these types of devices is seen below in Figure 6-1. By fabricating the resonator device first, the highest-Q factor devices can be produced, increasing device quality. Then, the 2D material can be grown or transferred onto the resonator. The images seen in the figure below indicate that 2D materials can be grown on microsphere resonators creating functional high-Q optical devices dressed in 2D materials. However, this work needs to be expanded upon. Initial experiments have
demonstrated that material transfer onto microresonator devices (microtoroids and microspheres) leads to very low throughput on the device manufacturing, and, although several modes were supported, the residue from the transfer process leaves a poor resonator surface quality. Growth based devices have had some success, generating devices with Q-factors over $10^5$, but resonant effects have yet to be witnessed in monolayer PL generation (shown below in figure 6-1).

Figure 6-1 Optical Microsphere Resonators with TMD Monolayers. a) Optical micrograph of a microsphere resonator with transferred exfoliated MoSe$_2$ flake. b) Optical micrograph of a microresonator with exfoliated WSe$_2$ flake. c) and d) PL images of microsphere resonators with grown WS$_2$ triangles.

In order to produce the best microresonator based devices, microresonators must be built smaller and have higher Q-factors (leads to a higher resonator $\beta$ factor)[109]. By reducing device diameter (thus decreasing growth surface area) and increasing resonator quality factor (decreasing
surface defects when growing 2D materials on microsphere resonators), 2D/microresonator systems could become high quality, narrow band micro-lasers. Further material enhancement, such as purifying the 2D material grown on the surface[110] or growing TMD alloys[33], can generate much higher PL intensities, leading to a more effective light emitting device.

In conclusion, 2D materials are promising materials for optical devices and applications. They have strong absorption, PL emission, and nonlinear generation all emanating from an incredibly thin crystal. Furthermore, by altering the thickness of these materials, their optical properties can be engineered to fulfill a wide variety of optical characteristics. This makes them an effective material to enhance preexisting optical systems that lack these optical qualities, such as SiO$_2$ based devices and systems. The first step to fabricate these devices is to characterize and understand the mechanisms that drive the strong optical reactions in these atomically thin materials. Much of this work is described in this dissertation. However, there is still much work to be done before the next-generation of optical devices is constructed by dressing systems with 2D materials.
Appendix – Tunable Laser Frequency Locking Algorithm

Because the fabricated microsphere resonators have extremely high Q factors, they are very susceptible to fluctuations in the resonator temperature. Both the material refractive index and the sphere radius increase when the resonator is heated, the mode of the resonator can wildly fluctuate with the resonator’s changing temperature[111]. This is seen in figure A-1, where a typical scan across several microsphere resonator modes are shown. In the figure, there is a sharp mode with a width of 10 MHz at approximately 9 GHz frequency shift both when scanning the frequency up and down using the piezo-actuator (driven by a function generator plotted in red). However, upon careful observation, the mode is not of the typical Lorentzian shape. When scanning the frequency up, the full-width-at-half-maximum resonance width of the mode is very small, approximately 4 MHz. This is not the actual resonance mode width (10MHz). When the pump approaches the resonance of the mode, the energy inside the resonator increases. This causes the microsphere to increase in temperature (due to very weak absorption), and thus, the optical path-length in the cavity increases due to the thermal expansion and refractive index increase. This causes the resonance frequency of the cavity to decrease, shifting it opposite of the pump frequency scan direction (Resonance Shift black arrows in Figure A-1). This causes the mode width to appear falsely shortened, as the two frequency shifts are of the opposite direction. This effect occurs in the opposite form when scanning the laser down in frequency. As the pump frequency decreases, it once again approaches the resonance frequency of the resonator. As the resonator field begins to increase, the temperature rises, causing the optical path length to increase and the resonance frequency to decrease. However, when scanning the pump down in frequency, the frequency shift of the pump is of the same direction as the resonator shift, falsely widening the mode with to 375 MHz full-width-half-max.
In order to correct for this thermal shifting, a complex system was designed to lock the pump frequency to the resonance frequency of the resonator (Figure A-2). In this system, two methods of control are allowed: mode scanning and mode tracking. Mode scanning allows for the scanning of the resonator modes to characterize the resonator utilized in the experiment (this results in the transmission spectra taken in Figure A-1). The mode tracking system allows for the laser frequency to be locked to the resonant peak of the mode, useful for taking Raman spectra or for generating lasing within the resonator due to the large built up field within the resonator. In order to switch between systems, two switchboxes were installed so that the system could easily be converted between either modes without losing time or unplugging cables.

The mode scanning system is generated from two frequency generators which are coupled to one another using the first generator as a trigger, and the second delayed by half the period. The first
generator is sent into the piezo-actuator driver, which magnifies the function generator signal by 10x. This allows the frequency of the pump to be tuned up to 24GHz, thus allowing high resolution transmission measurements. However, because the laser system is rarely stable across the entire tuning range, the laser current output must be corrected to prevent the laser from skipping in mode frequency. The root of this can be seen in the laser cavity path length equation, shown below in equation (A.1):

\[ L = d_c(V) + d_{ld} n_{ld}(I) \]  

(A.1)

Where \( d_c(V) \) is the path length in the external cavity and \( \Delta d_c \) is the additional length changed by the piezo-actuator. \( d_{ld} \) is the laser diode path length and \( n_{ld} \) is the refractive index in the laser diode. When using the piezo-actuator, the path length changes by a large enough amount that another frequency is more stable in the laser cavity than the original tuned wavelength. This causes the frequency of the laser to skip to the more stable frequency, causing a discontinuity in the output frequency scan[112]. This ‘mode skipping’ is a crucial problem that must be overcome for both microresonator characterization and locking the laser to the resonant mode of the resonator. An example of mode skipping can be seen in the indicated area in Figure A-1, where a sharp discontinuity occurs in the fiber transmission. In order to correct this, the optical path length through the diode itself can be altered. Although the distance the light travels cannot be tuned, the refractive index of the diode itself can be altered by the application of additional current, so that the index is then \( n_{td}(I) = n_{td} + \Delta n_{td}(I) \) where \( \Delta n_{td} \) is the refractive index change due to a change in the input current. By appropriately changing the refractive index in the cavity (amplitude on the second function generator), the mode skipping can be reduced and can be eliminated from the frequency sweep. In order to make the second function generator output the proper magnitude, the output is reduced by a 0.1x amplifier circuit; using this method, the full range of 22 GHz can be tuned without the mode skipping to another frequency. One careful note is that when tuning the laser diode current, the operational scanning range of the system decreases by 2 GHz (due to changes in the cavity
refractive index). However, the increased continuously tunable range is preferred, not only because of its continuity, but also because it has a consistent scanning range of 22 GHz (verified using an external Fabry-Perot interferometer across the tuning range of the diode).

The mode tracking system is more sophisticated than the scanning mode. First, the output of the first function generator drives the piezo-actuator driver, similar to the scanning mode. However, this first passes through an amplifier circuit, to reduce the voltage at the driver. If the slope of the fiber transmission signal is non-zero (any realistic case), this will cause a tiny oscillation on the output of the fiber transmission. This can be detected using a lock-in amplifier driven at the same
frequency as the function generator. The lock-in amplifier then generates a positive or negative value, depending on the slope. This signal is especially prominent when near a resonant frequency of the resonator, as the transmission slope is larger in this region. A computer program detects the sign of the lock-in amplifier output though a DAQ and uses this sign to calculate a DC voltage value. This DC value is then sent into the amplifier before the piezo-actuator driver, offsetting the voltage value from the function generator by the DC value. Similarly, the DAQ can output a voltage value to the laser current driver, correcting for the current in equation (A.1). By varying the DC voltage value, the laser frequency can track the resonant mode as it varies with temperature or through room fluctuations, allowing the Raman spectrum to be taken when frequency locked to the resonance of the microresonator.
References


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Selected Publications

Selected Conference Presentations and Proceedings