Optics of Two-Dimensional Materials used as Substrates for Nanoparticle-Based Devices

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Proposed Phase II for Small Business Innovation Research (SBIR) for Senior Design Group 3

Optics of Two-Dimensional Materials used as Substrates for Nanoparticle-Based Devices

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Abstract

With initial funding, Phase I of an investigation into enhancing optical properties of monolayers of transition metal dichalcogenides with the addition of nanoparticles was successfully completed. Exfoliation and initial rounds of atomic force microscopy were able to determine that monolayers could be identified, but there was a serious need for further study in a proposed Phase II. This proposed Phase II will allow for deeper studies into the enhancements of optical properties by nanoparticle additions and efficient crystal growth methodologies which could give rise to existing and novel applications. From this proposed phase, it is expected that large diameter nanoparticle coatings will allow for broader absorption and scattering as well as a red-shift that will in turn enhance the optoelectronic properties already existing in the transition metal dichalcogenides. This, in combination with lower temperatures that increase the effectiveness of monolayer growth in crystals, will provide greater insight in how this combination can be used for future applications. This study’s materials and results will have the capability to improve and develop many applications such as but not limited to piezoelectric materials, biosensors, and photodetectors.

Optics of Two-Dimensional Materials used as Substrates for Nanoparticle-Based Devices

Due to great successes coming from the funding of the SBIR Phase I grant, MSE 489 Group 3 proposes an addition of a Phase II that will allow for a continuation to build off of the highly successful exploratory research into the optics of two-dimensional materials used as substrates for nanoparticle-based devices. Before further ideas and funding can be proposed and discussed, an update of Phase I’s exploratory research, testing, and results will be presented and explained. The proposed methodology, expected results, and plans for future work stemming from the Phase I results will be proposed as Phase II. Phase II methodology and theory is then discussed in great detail for funding purposes. This study is expected to produce insight into the material properties of monolayer transition metal dichalcogenides with nanoparticles that will assist in the development of future studies and novel applications. Specific applications that would benefit from research in this study could possibly include biosensors, photodetectors, and piezoelectric materials.
1.0 Phase I Background Study

In recent literature, transition metal dichalcogenides (TMDs), have been looked into as promising materials for the development of advanced properties in several applications [1]. Three of the biggest applications currently being investigated are optical, electronic, and mechanical devices. However, with these advancements in technology, some fundamental issues have also been discovered. One, if not the most promising TMD for these potential applications, Molybdenum disulfide (MoS$_2$), is extremely sensitive and reactive to gases in the environment. When MoS$_2$ comes in contact with the surrounding gases, the original optical and electrical properties that were observed become modified. Previous studies have shown promising ideas by producing some sort of coating to apply to the surface to prevent contact with outside gases [1]. To build on this concept, it is proposed that a nanoparticle coating of a material such as gold or silver would not only prevent modifications to the TMDs, but it could also further enhance these studied properties. To be able to understand and enhance these investigated properties, a fundamental basis of knowledge is needed on the various materials and techniques that will be used and evaluated in this study.

1.1 Transition Metal Dichalcogenides

Transition metal Dichalcogenides (TMD) have shown great potential in electronics and energy storage applications. Monolayer TMDs are 2D nanomaterials consisting of a single layer of a transition metal between two layers of chalcogen atoms. These atoms are typically selenium, telluride or sulfur. For this experiment molybdenum and tungsten will be the transition metals used and the chalcogen atoms will consist of sulfur and selenium. Molybdenum disulfide (MoS$_2$), molybdenum diselenide (MoSe$_2$), tungsten disulfide (WS$_2$) and tungsten diselenide (WSe$_2$) are semi-conductive crystals that each exhibit unique properties on a 2D level and could be valuable for testing in this experiment. All these materials have a melting temperature that is greater than 1000°C and are stable and inert at room temperature [2]. They also exhibit weak interactions in 3D space, which allows for them to be easily exfoliated to achieve a monolayer thickness [3]. While each of these crystals have been developed to show great promise in this field, the primary focus for this study specifically will be MoS$_2$.

At the monolayer level, the crystals are flexible in this dimension and will have direct band gaps between 1.0 eV and 2.0eV [2, 3]. It has been shown that by varying the thickness, the band
gap structure can change from an indirect to a direct band gap. The 2D TMDs have also shown a large bandwidth of light interaction that ranges from infrared to ultraviolet wavelengths. Single layers of these crystals present good absorbance properties, with the ability to absorb almost 10% of light in the visible spectrum. This absorbance property is due to the interaction of light and matter in the semiconductor monolayer. The structure of these TMDs has been shown to have 1000 times the photoluminescence intensity of the bulk structure due to the direct band gap present [4].

1.2 Crystal Growth

Several methods can be used to produce bulk TMD crystals. One such method is chemical vapor transport (CVT), which utilizes the instability of the elements to help facilitate the necessary chemical reactions to produce the TMD crystals deposited as a 2D layer within the reaction temperature range. This growth method uses a sealed tube under vacuum along with a stoichiometrically-accurate pressed pellet of material that will grow into a crystal in a furnace for several days before being allowed to cool. However, this method also has risks of contamination of the crystals. TMDs should be of the highest possible purity to ensure correct properties and behavior, so it is important that these impurities are kept to a minimum. Another method is chemical vapor deposition (CVD) which involves growing a crystalline film on a substrate. During CVD, a chemical reaction using a gas produces a single or thin film that is deposited onto the substrate surface. Varying environmental conditions such as substrate material, temperature, and gas composition will produce an array of varying properties of crystals [5]. These processes of producing TMDs allows for the study of the properties of these materials in a 2D state (post-exfoliation) as well as allowing for additional steps to examine the unique properties of the TMDs [7]. For the purpose of this study, CVD will be focused on in methodology and results of Phase II.

Fig. 1. Layered structure of an MX2 TMD material. Here M is a transition metal and X is a chalcogen. The X-M-X tri-layers are separated by van der Waals gaps. The weak bonding between these tri-layers enables exfoliation into single layers [5].
1.3 Exfoliation

Micromechanical exfoliation is a technique that is used to create very thin flakes of a crystal and can be used to create few-layer or monolayer specimens. This is possible because of the weak van der Waals interactions which bind the layers together and that facilitate the cleavage of the material [8]. Therefore, this is only possible in materials that exhibit a layered construction wherein the crystals form strong covalently bonded layers, i.e. two-dimensional layers, that bond together via these weaker interatomic forces. An example of this structure can be seen in Fig. 1. These weakly bound layers can be pulled apart using low levels of force. This can be achieved by using the mechanical force which results from peeling off the crystal layers with adhesive tape. While other tapes can be used, the typical adhesive tape used for this technique is Scotch tape.

1.4 Plasmonic Nanoparticles

Plasmonic nanoparticles are a type of nanoparticle that have been shown to exhibit properties which enable the fine-tuning of a material’s optical and electronic properties when deposited on its surface. These particles, typically made of gold, silver, or platinum, have been shown to undergo a collective oscillation when excited by light at specific wavelengths known as a surface plasmon resonance (SPR). This phenomenon generates a strong interaction with light that allows the plasmonic nanoparticles to absorb and scatter light with great efficacy [9]. The diameter of the nanoparticle plays an important part in determining its optical properties. Fig. 2 shows the relationship between wavelength, optical density, and diameter size of gold and silver nanoparticles. As can be seen, small gold nanoparticles absorb light and larger particles have

![Fig. 2: The extinction spectra of gold (2A) and silver (2B) related to particle diameter.][9]
broader peaks and scatter light. The larger gold particles scatter more light because as their size increases, so does the albedo and cross-sectional area as well. The same correlation between particle diameter and absorption can be seen in silver nanoparticles, except the smaller particles have peaks near 400 nanometers whereas gold particles have peaks close to 520 nanometers. The accumulation of nanoparticle clusters can also be seen to affect optical properties. As the particles begin to accumulate, the conduction electrons are shared between surrounding nanoparticles and become delocalized. This results in a shift in absorption and scattering peaks to longer wavelengths because the SPR moves to lower energies [9].

2.0 Phase I Methodology

2.1 Exfoliation

To create 2D monolayers from the grown TMD crystals, micromechanical exfoliation via Scotch tape is used to pull thin flakes off the surface of the crystal. The thin flakes on the tape consist of varying thicknesses of 2D layers, often up to several hundred layers of 2D molecules [6]. The tape is repeatedly used to peel off thinner and thinner flakes of the material, dividing the number of layers roughly into two sections each time the tape is peeled back as can be seen in Fig. 3.

Once sufficiently thin flakes are present on the tape, a section of crystals is identified which contains a variety of shapes and thickness and may present ample opportunity to find monolayer TMD crystals. This section of the tape is then placed adhesive-side down onto a silica substrate which has been polished, cleaned, and made hydrophilic. Pre-polished surfaces were obtained and then treated with oxygen plasma to clean the surface and make it hydrophilic. The area of the tape in contact with the substrate is gently pressed and held to ensure the adhesion of layers. The substrate and tape are then gently heated, and the substrate is peeled away from the tape. This leaves an extremely thin layer of material on the substrate in which several areas can hope to be identified as a monolayer using a microscope.
The presence of 2D crystallites can be seen under an optical microscope at very high magnification. Single-layer crystals are typically seen in conjunction with other atomically thin crystals (ranges are typically between 2 and 5 atomic layers) and appear nearly transparent under the microscope. While these thin crystals would be more visible using scanning electron microscopy (SEM), optical microscopy will be used to identify these segments of crystal due to ease of use and time needed for equipment.

2.2 Atomic Force Microscopy (AFM)

After monolayer identification, atomic force microscopy (AFM) will then be used to confirm the single-layer or few-layer thickness of the TMD crystals. AFM utilizes an extremely small cantilever and optical measurement system to trace the topography of a sample, shown in Fig. 4. As the cantilever is traced across the surface of the material, the potential energy between the tip of the cantilever and the surface of the sample induces a $z$ component of force on the cantilever and causes it to deflect, which can be seen in Fig. 5 [12]. This deflection is most commonly observed by measuring the deflection angle of a light source off a reflective surface on the cantilever. Deflection measured in this way can have resolutions of $10^{-4}$ Å, much smaller than the average spacing of a crystal lattice, which can be used to topologically map the surface of the material [11]. The purpose of using AFM in this work is to characterize the thickness of the crystallites produced by micromechanical exfoliation. Once it is confirmed that we have produced few or monolayer crystals, the optical properties of the crystals will be able to be characterized. For these experiments, no more than 5 atomic layers can be utilized to be able to conduct these characterizations to keep these studies in the 2D or thin film regime.

**Fig 4:** An example schematic of an AFM. This schematic shows the basic reflectance setup for a traditional optics-based AFM [11].

**Fig 5:** The tip of an AFM cantilever near the surface of a sample. The sample tip interacts via Coulombic forces to produce the highly sensitive AFM height maps [12].
3.0 Phase I Results

3.1 Exfoliation of MoS$_2$

Using the methodology provided above, exfoliation was performed multiple times on specimens of graphene and MoS$_2$. Graphene samples were created as practice specimens, as it is relatively cheap and much easier to produce monolayer samples from. This being said, these specimens will not be included in the final results. In total, two graphene and six MoS$_2$ samples were created. Confirmation of successful thin film production was conducted by optical microscopy and AFM and is described in detail below.

3.2 AFM Thin Film Identification

Several optical micrographs of MoS$_2$ samples post-exfoliation can be seen in Fig. 6. The images show several exfoliated crystallites which can be identified as the well-defined shapes with clear-cut edges. Residual residue left over from the adhesive tape can also be seen in the image as unclear, “smudged” objects. As can be seen from the figure, most of the crystallites have a white, opaque appearance. Some of these crystals, however, show blue hues and appear to be slightly translucent. Because the light from the optical microscope seems to be visible through the crystallites, these are believed to have fewer atomic layers when compared to the opaque crystallites. This is additionally supported by the slight blue color of the translucent crystallites, which is the result of phase interference generated by internal reflections of light being out of phase with the initial light source. Darker blue color of the crystallite is believed to therefore coincide with thinner crystallites or fewer atomic layers. However, as specimens get closer to monolayer thickness, they appear more translucent on the microscope. Because more white light can pass through these thinner samples, the light source remains visible through the crystallites. As such, the crystallites are believed to have a higher concentration of atoms or a lower layer thickness. This is supported by the observed blue interference colors in the images, indicating a phase difference in the light passing through the crystallites.

![Fig. 6: Optical micrographs of thin film specimens of MoS$_2$.](image)

Both images taken at 1000x magnification. Images show crystals of varying thickness, evident from blue interference colors.
through the specimen, the blue color gets lighter and the sample becomes more transparent. Monolayer crystal samples were expected to appear especially translucent with a slight blue color. Examples of crystallites found that were expected to be monolayer are labeled in the figure above.

Using the data gathered from the images above, AFM was conducted in the area believed to contain monolayer thin-film crystallites of MoS$_2$ in Fig. 6(a). The scan area and the resulting height map can be seen in Fig. 7. It can be seen from the figure that extremely thin crystallites were present in the scan area, on the order of magnitude of tens of nanometers. While this is very thin, it is still much larger than the 6.15Å thickness which would represent a single layer of MoS$_2$ [13]. Additionally, the targeted area which was believed to be monolayer does not appear in this scan. The authors believe this is most likely due to the large elevation difference between the target and the adjacent crystallite. As shown in the figure, the neighboring crystallite is roughly 80nm in height, more than 100 times the height of a monolayer. This large difference likely caused the monolayer to be overshadowed in the scan.

However, attempts to further isolate the potential monolayers were unsuccessful because of the extremely small size of the crystallites. It is believed that further exfoliation of the specimens prior to measurements would create larger, thinner, and more easily accessible crystallites which could be examined using AFM with ease. Theoretically, roughly half of the atomic layers should be stripped away from the crystallites upon each subsequent exfoliation. Repeated exfoliation, therefore, should create more thin film candidates while also reducing the height of other crystallites, allowing AFM to more accurately scan the samples. Due to limitations in timing and
funding for this section, a more thorough continuation of this work is proposed as a part of Phase II of this project.

4.0 Need for Phase II

While initial difficulties occurred during AFM analysis of the created monolayers, Phase I proved that studies can and need to be furthered to investigate the optical properties that these monolayer crystals possess. Not only does this exploratory study examine the optical properties of the TMD crystals themselves, but it also gives rise to the idea of enhancing the already promising optical properties of these crystals with the deposition of gold plasmonic nanoparticles. Various crystal growth techniques, further in-depth AFM examination, and comparisons of the optical properties with addition of nanoparticles will be examined in full during the proposed Phase II of this study. Future work is also needed to reveal the possible enhancements of optical properties and methodologies that contribute to the development of biosensors, photodetectors, and piezoelectric applications.

5.0 Phase II Proposed Methodology

5.1 Continuation of AFM

As a first step in Phase II, primary focus will be placed on reevaluating the techniques used to collect AFM measurements that will be able to confirm that monolayer thin-film specimens have been produced. As discussed earlier, it is believed that furthering the exfoliation process of the specimens prior to AFM would enable more accurate topology measurements of monolayer sections of the crystal. Indeed, according to literature on the topic, continued exfoliation of van der Waals crystals leads to increasingly thin specimens [8]. Upon the confirmation that mechanical exfoliation did produce monolayer thin specimens, further characterization and evaluation of optical properties can be conducted.

5.2 Characterization and Optical Properties

Once AFM has been used to confirm that atomically thin layers of crystals were in fact obtained from exfoliation, a myriad of optical properties will be explored. The main optical property that will be examined in this work is absorption. Should ample time and funding be present, scattering and reflection will also be studied.
Absorption will be characterized using an absorption spectrometer. A glass prism will be used to disperse white light into its different constituent colors to characterize the specific wavelengths of transmission and absorption for the samples. When the sample encounters light, various amounts are reflected (R), transmitted (T), and absorbed (A). This concept is expressed in the following basic equation: \( R + T + A = 1 \). A spectrometer will be used to absorb the light passing through the sample and produce an optical density curve for this light. A reference curve will be established using the transparent silica substrate as the reference. The 2D TMD crystal will then be deposited on the substrate and the spectrometer will be used to graph a new optical density curve. Subtracting the reference curve from the crystal-substrate curve will yield the absorption spectrum of the crystal. The absorption spectrum of the TMD thin film, the plasmonic nanoparticles, and the TMD with nanoparticles deposited on the surface will be measured in this way [14].

A collimated laser will be used to characterize the scattering of the samples. The laser will be positioned to travel through the dichalcogenide. If the projected light appears dark or is “scattered” then scattering has occurred which will mean the dichalcogenide was grown incorrectly. Scattering should not occur within the dichalcogenides because scattering occurs when light interacts with objects that are roughly the same size as the wavelength of the light. As visible light (ranging from 400 to 700 nanometers in wavelengths) will be used in this work, the dichalcogenide and nanoparticles used (both 15 and 50 nanometers will be evaluated) will interact minimally with the light and should not yield any characterizable scattering [14].

To observe reflection of the 2D TMDs, a micro-reflectance spectrum needs to be acquired by an epi-illuminated mode on a microscope. By closing the aperture of the microscope to close to around 60 micrometers in diameter, the stray light will be able to be collected by a finite numerical aperture of an objective lens. A transmittance spectra can be seen in a similar way. The 2D TMD crystal will be deposited onto the end facet of the fiber bundle to be observed with other lenses allowing for visualization of the micro-reflectance spectrum [14].
5.3 Deposition of Gold Nanoparticles

Following the various optical testing of the crystals, gold nanoparticles will be deposited from colloids onto the 2D crystals using solvent evaporation or spin coating. Gold nanoparticles are in a colloidal liquid form with a solvent containing the nanoparticles in a uniform density of particles throughout the colloid. Two sizes of nanoparticles (15 and 50 nanometers) will be used to explore the plasmonic effects of nanoparticles on TMD optical properties. Previously studied literature has shown that the larger nanoparticles will tend to exhibit increased scattering compared to the smaller nanoparticles, while the smaller nanoparticles should result in increased absorption in the Visible-UV spectrum [15]. It has also been shown that the size of the nanoparticles will also affect the refractive indexes. The optical properties will in turn be affected by how the gold nanoparticles will aggregate. The deposition of the nanoparticles will be characterized via SEM. The spin coating of nanoparticles will be conducted and evaluated for the deposition of gold and possibly silver on the crystals.

Spin coating is often used to apply thin layers of a material onto a substrate. This occurs when a solution of the material and solvent are spun quickly and covers the surface evenly. The centrifugal force generated by the spinning coupled with the liquid solution ensures the surface is evenly coated as shown in Fig. 9. This method is an easy and quick way to produce a thin and evenly distributed film of nanoparticles onto the silica substrate [16].

It has been shown that the areal density of the subject which is coated in nanoparticles will directly impact its optical properties and performance [17]. The areal density will be determined using SEM imaging and the particle analytics and thresholding functionality of ImageJ. As could be expected, increasing nanoparticle density will increase the effect of the particles on the properties. Thus, higher areal density should lead to increased absorption, scattering cross section, and other properties. As areal density is not the primary focus of this study, consistent nanoparticle deposition will be a critical in ensuring uniform measurements are taken. Consistent timing and mixing of the techniques described above will be used to ensure an even areal density across the examined surfaces.
5.4 Reexamination of Optical Properties

Following the deposition of the gold nanoparticles onto the surface of the 2D TMDs, the optical properties will then be reevaluated for any observable changes. The properties that will be retested will be absorption, and scattering and reflection if time and funding permit. Comparing the optical data pre-deposition to the data post-deposition will allow the determination of how the TMD optical properties were affected by the gold nanoparticles. Each method for the various properties will be repeated following the exact manner performed originally on the pure TMD crystals to ensure that the changes in optical properties only occur due to the nanoparticle addition and no other outside interference. Each property will be recharacterized such that the dataset includes the 2D crystal, the plasmonic nanoparticles, the 2D crystal with deposited nanoparticles, and a reference curve (the transparent silica substrate).

5.5 Crystal Growth

This crystal growth process will be performed with optical testing of purchased crystals to then have the capability to determine if there are any differences in optical qualities of grown verses purchased crystals. The crystal growth process will consist of two parts, pellet forming and chemical vapor transport. In the former, each component must be weighed out and ground in a mortar and pestle to form a fine powder. This allows the specimen to form a single-phase, polycrystalline specimen in the furnace. The mixture will then be formed and pressed into a pellet using a hydraulic press as shown in Fig. 10 [18]. Each pellet will be weighed and is approximately 3 grams. It is important to ensure the levels of sulfur in the samples are correct, as elevated levels could lead to an explosion in the sealed tube while in the furnace. Once the pellet is made into a single-phase, polycrystalline specimen, it is reground to powder and properly sealed within the

![Fig. 10](image_url): A cartoon diagram displaying the powder compaction of a green body part [18].
quartz tube along with a small amount of iodine. Maximizing the volume of the tube will aid in preventing an explosion upon heating. Once sealed, the tube is placed in a tube furnace which is between 700-1050 °C and has a temperature gradient of roughly 50°C from the hotter center to the colder edge. This gradient facilitates chemical vapor transport in the tube and allows for single-phase, monocrystalline samples to be grown. Effect of temperature on TMD crystal properties will be examined by manipulating the temperature at which the crystals are grown. By evaluating these various temperatures, it is hoped to have the ability to achieve greater efficiency in creating these TMD crystals. This could then lead to the possibility of removing some of the extra exfoliation processes that occur before the deposition of crystals onto the substrate.

6.0 Expected Results of Phase II

6.1 Different Crystal Results

While there is currently no known research regarding the benefits of using grown crystals as opposed to buying crystals from a supplier, personally growing crystals allows for greater control of variables and crystal properties. During crystal growth, the environment in which the crystal is grown in will be manipulated to determine possible effects on crystal thickness and optical properties. In particular, the temperature will be changed during the growing process. Current research shows that altering this condition can produce different types of MoS\(_2\) crystals. It is thought that the change in this parameter will result in different nucleation methods during crystal growth which then explains why different types of MoS\(_2\) crystals are produced at various growth temperatures. For the selected crystal growth method of chemical vapor deposition, temperatures at each end of the spectrum (both low and high) will be chosen to grow and analyze the effects on the crystals. It is expected that the lower temperature range (725°C-775°C) will produce thinner flakes that are triangular in shape. This lower temperature range allows for slower, more uniform growth of monolayers. Similarly, we expect the higher temperature range (850°C-925°C) to produce triangular but thicker MoS\(_2\) flakes. A schematic of the triangular shaped crystal can be seen in Fig. 11. As can be seen in the figure, the shape of the MoS\(_2\) crystal evolves from a circular shaped nucleus to its known triangular shape during crystal growth. The quicker growth that occurs at

![Fig. 11: Graphic of the transformation of MoS\(_2\) from a nucleus to a flake during crystal growth [19].](image-url)
higher temperatures is more likely to produce multilayers of MoS$_2$ that could likely reach thicknesses in ranges of 15 to 20 layers thick [19]. These results will be determined using AFM image analysis, and if the results present are as expected, experimentation of optical properties will continue focusing on the lower temperature grown MoS$_2$ crystals.

6.2 Continued AFM Results
A diagram of the expected results is shown in Fig. 12 [20]. Fig. 12(c) shows a height map as gathered by AFM along the scan path displayed in Fig. 12(b). The change in height across this crystallite is shown to be 6.75Å, which is roughly the theoretical value of the thickness of monolayer MoS$_2$. As can be seen from Fig. 12(a), the optical micrograph of this crystallite appears translucent with a slight blue color, similar to the results gathered in Phase I. Continuing the mechanical exfoliation is expected to produce larger monolayer crystallites like the one that can be observed in the figure. Due to the similarity between the thickness of the observed crystals and values in the literature, it is believed that successful production of monolayer crystallites was achieved in Phase I. However, further AFM characterization is desired to ensure the validity of this hypothesis and will be the initial research focus for Phase II.

6.3 Optical Properties of Crystals
A study done in 2012 investigated the Raman scattering of thin-film MoS$_2$ crystals in a continuing effort to characterize the material’s optical and electronic properties [21]. Raman spectroscopy can be used to identify various vibrational modes which result from a crystal

![Fig 12: Optical micrograph (a), AFM image and scan path (b), contact map and height map (c) of an MoS2 monolayer crystal. The height map in (c) shows the rough height of the monolayer sample to be around 6.75Å, or just slightly larger than the theoretical MoS2 monolayer height. Crystals looking similar to the one shown in (a) were search for as candidates for monolayer crystallites [20].](image)
structure. By measuring the Raman shift, the stiffening (increasing shift) and relaxing (decreasing shift) of the vibrations can be characterized. In MoS$_2$, two prominent Raman scattering modes are $E_{12g}$ (in-plane S-S vibrations with respect to Mo) and $A_{1g}$ (out-of-plane independent S vibrations in opposite directions) [21]. Fig. 13 shows the Raman shifts of these modes with varying layer number and shows the $E_{12g}$ mode decreasing and the $A_{1g}$ mode increasing with increasing layer count. This stiffening of the $A_{1g}$ mode is caused by vibrational suppression from interlayer van der Waals forces resulting from more atomic layers [21]. The deposition of nanoparticles onto the surface of thin-layer MoS$_2$ is estimated to have a similar impact but to a lesser degree. Interaction forces between the nanoparticles and the thin-film could suppress the out-of-plane vibration of the S atoms. Thus, the shift in this scattering mode could be used to characterize the effect of nanoparticles on the scattering properties of the device. As plasmonic nanoparticles have been shown to exhibit excellent scattering properties [9], it is expected that the total scattering cross section of these devices will significantly increase after the deposition of the nanoparticles, observed as a general increase in scattering intensity peaks. Stiffening of the $A_{1g}$ mode as a result of the interaction forces between the MoS$_2$ and the nanoparticles is also expected.

2D TMDs have attracted an enormous amount of interest due to their relatively high absorption coefficient. One investigation has shown that the average absorption coefficient for a 2D MoS$_2$ sample is approximately $2.8 \times 10^6$ cm$^{-1} \pm 0.13 \times 10^6$ cm$^{-1}$ [22]. Following the deposition of the gold nanoparticles, the absorption coefficient will be retested for each sample. After retesting, the absorption coefficient values is expected to have increased as a result of the deposited nanoparticles increasing the overall absorption for a particular wavelength.

Another investigation discussed is the double resonance Raman process in 2D materials focusing on MoS$_2$ dichalcogenides. The purpose was to highlight the origin of the bands mediated
by the two-phonon and phonon–defect processes and find guiding principles for the appearance of double resonance bands. The authors state that the double resonance bands observed within transition metal dichalcogenides are due to intervalley scattering [23]. For MoS$_2$ a transition from indirect to direct band gap occurs upon the reduction from bulk to monolayer. Due to a strong spin–orbit coupling, a split in the valence band occurs and gives rise to the excitonic transitions named A and B. Fig. 14 shows the transition from indirect to direct band gap in the electronic dispersion of MoS$_2$ and the Raman spectra of monolayer MoS$_2$ collected at different laser energies across the A and B excitons is shown in Fig. 15 [23]. The results experienced by the studies researched above are expected to be closely mirrored by this study.

It is expected from research of prior studies that the micro-reflectance of MoS$_2$ will show reflections around wavelengths of 1.90 eV and 2.05 eV. These observations tend to agree with previous photoluminescence studies [14]. Valence band will then be split because of a strong spin-orbit interaction due to the atoms creating two direct band gap transitions. This spectra is also expected to show a broad feature around the 2.85 eV range and a red-shift will in turn be expected as well. These results can be expected to originate from singularities in the joint density of states between the valence and conduction bands and lead to optical transitions that are nearly degenerate in energy. Another expected result is that the quantum yield between monolayer and multi-layer crystals of MoS$_2$ will decrease by a factor greater than 1000 times. Future work from this reflectance study would have the capability to influence more studies investigating these properties of conduction and insulation without excitonic features [14].
6.4 Optical Properties of Crystals with Nanoparticles

Due to the plasmonic interactions of gold nanoparticles, it is expected that the absorption of the system will increase as a whole. Literature has shown that the absorption will most likely increase with the deposition of nanoparticles, but that the absorption peak may also shift slightly as well [15]. It was demonstrated that 2D MoS$_2$ coupled to gold nanoparticles in solution saw a slight increase in the extinction peak of the absorbance curve [9]. In addition to this increase of the extinction peak that is observed, it is also thought from prior research and studies that in general, a greater ratio of gold nanoparticles to MoS$_2$ leads to a growing absorption. It was then determined in accordance with this ratio that if the sizes of nanoparticles were less than 10 nanometers, the plasmonic spectra would not be visible [24]. Therefore, based upon this research, in the specific comparison between the 15 nanometer and the 50 nanometer gold particles in this study, it will be expected that the larger 50 nanometer particles will exhibit increased extinction over the 15 nanometer particles [3]. These results support the possibility of optoelectronic properties. The properties are advanced by the suppression of the SPR leads to a delocalization of plasmon electrons. With this phenomenon and the fact that the nanoparticles can produce their own SPR, a collective plasmon oscillation is expected to be produced [24]. While the main focus on the evaluation of optical properties for this study was on absorption, smaller investigations and results were collected to look into the reflective and scattering properties of this combination.

For scattering properties, based upon prior research and studies, it is generally expected that as the size, distribution and aspect ratio of nanoparticles increases, the scattering peak will become broader and more red-shifted which is very similar to the ideas shown in absorption. It is also thought that with scattering, the plasmon bandwidth will increase as the interaction of the wavelength of light becomes comparable to that of the dimensions of the nanoparticles [25]. Due to information from previous studies, it is expected in this experiment that a peak will be seen around the 700-800 nanometer mark that is not normally observed in MoS$_2$. Fig. 16 showcases this peak that will be expected

![Fig. 16](image_url)

**Fig. 16:** The new peak not normally seen in MoS$_2$ can be observed around 700-800 nm with addition of gold nanoparticles affecting the plasmon resonance [25].
due to its dependence on the size and shape of nanoparticles to affect the plasmon resonance [25]. While reflective properties may be able to be observed on monolayer crystals, there is little research currently focusing on reflection as it changes with the addition of gold or silver nanoparticles. With the information on absorption and scattering from the studies that have been described and the expected results of this study, it would be presumed that reflective properties would show similar features. As absorption increased, it would seem logical that reflective properties would therefore have to decrease. The results of the prior studies and presented work, will reveal favorable properties from the combination of these crystals and nanoparticles that can then be used in several applications and lead to future studies.

7.0 Timeline for Phase II

While a Phase II for this experimentation was not originally expected, the minor setbacks experienced can be remedied by the proposed Phase II. This set of experiments in this phase can be broken into basic stages of crystal growth, crystal characterization, nanoparticle application, and final characterization. Crystal growth should allow for 2 weeks to create adequate samples of MoS$_2$ that will then be evaluated. After sufficient crystal growth has been attained, the crystals should be exfoliated and prepared for optical and electronic characterization. Optical and electronic characterization will include optical microscopy, atomic force microscopy, collimated laser, absorption spectrometry, and conductivity testing. Preparation and subsequent characterization of all crystal compositions should take place over the course of 2 weeks to allow suitable time for accurate identification and characterization of the 2D regions. The following 2 weeks will be used for nanoparticle deposition and recharacterization. This will consist of the deposition of silver and gold nanoparticles of varying sizes using the solvent evaporation and spin coating methods and repeating the tests conducted prior to nanoparticle deposition. Because of the already extremely successful basis that has been established in Phase I of this study, this set of experiments in Phase II should not need more than 6 weeks to complete, barring any delays for material or equipment acquisition.

8.0 Future Work and Applications

Following this Phase II, progress on the optical and electronic characterization of TMDs and deposited nanoparticles will be continued to test the impact of several variables including but
not strictly limited to TMD crystal composition, nanoparticle presence, nanoparticle size, nanoparticle composition, and nanoparticle deposition method. These variables could strongly impact the interactions between TMDs and the respective nanoparticles. Optical characterization to ensure the presence of a monolayer and determine absorption, reflection, and scattering would continue using optical microscopy, atomic force microscopy, columned laser, and absorption spectrometer. In addition to optical characterization, electronic characterization would take place to determine the impacts of the same variables in addition to temperature on conductivity of TMDs. Following these further characterizations on the TMD, MoS$_2$, other characterization on similar TMDs, such as molybdenum diselenide (MoSe$_2$) or tungsten disulfide (WS$_2$) for example, would also be investigated to determine if the same results present themselves. Results from this study and these discussed studies on other TMDs would then have the capabilities to be inserted into investigations on various applications mentioned such as biosensors, photodetectors, and piezoelectric materials.

The unique electronic and chemical properties of TMDs have made them an emerging material for many new applications. Research is currently being conducted on the ability of monolayer TMDs with nanoparticles to be used as a clinical diagnostic tool or targeting proteins and biomolecules for disease therapy. An example of usage for a MoS$_2$ biosensor can be seen in Fig. 17. This image shows a biosensor that is being used to drive a motorized syringe pump [26]. The high surface area of 2D TMDs allow for increased adsorption of proteins and other biomolecules as well as its fluorescent quenching ability that make it a promising material in the biomaterial field [27]. These unique and diverse properties also make it a favorable material for use in photodetectors. Photodetectors are currently utilized in a wide array of applications such as electronics, spectrometry, and imagining sensors. Many current detectors are made from silicone based materials, but their limited band gap hinder its application in infrared photodetection. The optoelectronic properties of TMDs with their ability to provide spectral coverage from infrared to visible wavelengths make them a favorable addition to this type of technology [28].
application of TMDs is piezoelectric detectors. While bulk TMDs do not have piezoelectric properties, the monolayer 2D crystals are able to exhibit a piezoelectric effect. The characteristics of these monolayer materials make them applicable to sensors that measure change in pressure, temperature, and strain [29]. Each of these applications has the ability to be enhanced based upon the results from this study. These results have the capability to also improve and potentially create other novel applications not previously discussed.

9.0 Conclusion

With the proper funding and ability for continuation into Phase II, MSE 489 Group 3 expects to be able to accomplish and finalize the various testing of TMD monolayer crystals with and without nanoparticle additions. With these finalizations, the expected enhancement of absorption and scattering following the deposition of larger diameter nanoparticles onto the monolayer of MoS$_2$ is expected to be observed in full. Following these discoveries, further investigation into differences in crystal growth are expected to produce results showing lower temperature growing conditions will allow for more effective techniques to produce monolayers. This group expects that with the funding and continued support, these advancements and discoveries will have the capability to present greater knowledge on developing biosensors and photodetectors that can fully utilize the increase in optical and electric properties.

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References:


