The Pennsylvania State University

The Graduate School

Eberly College of Science

# FUNCTIONALIZATION AND CHARACTERIZATION OF TUNGSTEN DISULFIDE WITH 2-AMINOETHANETHIOL

A Thesis in

Chemistry

by

Amisha Jinandra

© 2018 Amisha Jinandra

Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science

May 2018

The thesis of Amisha Jinandra was reviewed and approved\* by the following:

Mauricio Terrones Professor of Physics, Chemistry and Materials Science & Engineering Thesis Advisor

Raymond Schaak DuPont Professor of Materials Chemistry

Joshua Robinson Professor of Materials Science and Engineering

Thomas E. Mallouk Evan Pugh University Professor of Chemistry, Biochemistry and Molecular Biology, Physics, and Engineering Science and Mechanics Head of the Chemistry Department

\*Signatures are on file in the Graduate School

### ABSTRACT

Two-dimensional (2D) layered transition-metal dichalcogenides (TMDs) are an emerging, fascinating class of nanomaterial with a wide range of potential applications including catalysis, electronics, photonics, energy storage, and sensing. Although, highly crystalline TMDs are considered challenging to functionalize, owing to their inert nature. This work demonstrates that mono-layered or few-layered chemical vapor deposition (CVD) grown Tungsten Disulfide (H phase- WS<sub>2</sub>) can be functionalized via aerosolized thiolated ligands such as 2-Aminoethanethiol (NH2CH2CH2SH). The TMD materials were characterized before and after exposure to these ligands using Optical Microscopy, Fluorescence Microscopy, Raman Spectroscopy, Atomic Force Microscopy (AFM), Xray Photoelectron Spectroscopy (XPS), and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Adsorption of the sulfur bearing molecules on the surface of the 2H- WS<sub>2</sub>, with some selectivity relative to defective regions, was noted. However, it was determined that the thiol functional group was reduced on the surface to form a disulfide. This method of surface functionalization of 2D  $WS_2$  may provide an ideal platform in which the interaction between ligands and the 2D-TMDs may be used as selective anchoring sites that could result in the synthesis of novel functional materials.

## TABLE OF CONTENTS

List of Figures	V
List of Tables	ix
Acknowledgements	vii
Chapter 1 Introduction	1
<ul> <li>1.1 Transition Metal Dichalcogenides</li> <li>1.2 Defects in TMDs</li></ul>	1 2 5 7 7 10 13 16 18
Chapter 2 Functionalization of WS <sub>2</sub>	22
<ul> <li>2.1 Growth of WS<sub>2</sub></li> <li>2.2 Functionalization of WS<sub>2</sub> Monolayers</li> <li>2.3 Characterization of WS<sub>2</sub> Monolayers</li></ul>	22 24 26 31 34 41 46 47 48 51
Chapter 3 Conclusion and Future Outlook	52
<ul><li>3.1 Mechanism and Implications</li><li>3.3 Bibliography</li></ul>	52 58

## LIST OF FIGURES

Figure 1. Structural poly-types of pristine TMD layers. Chalcogen atoms are shown in yellow, and transition metal atoms are shown in blue. (a) The 1H phase, (b) the1T phase, (c) the distorted 1T, or1T' phase, (d) the 2H phase, (e) the 3R phase. <sup>4</sup>
Figure 2. Categorization of defects in two-dimensional TMDs by defect dimensionalities. TMD defects are classified by scale spanning (a) zero-dimensional, (b) one-dimensional, and (c) two-dimensional in structures. <sup>5</sup> 2
Figure 3 Atomic-resolution annular dark field (ADF) images showing different types of vacancy and vacancy complexes in MoS <sub>2</sub> monolayers. These zero- dimensional point defects involve single or multiple sulfur vacancies, or sulfur vacancies conjugated with a molybdenum atom or molybdenum vacancy. <sup>6</sup>
Figure 4. Grain boundaries in the 2D WS <sub>2</sub> , grown by CVD, are preferentially oxidized by controlled heating in air <sup>14</sup>
Figure 5.Graphical representations of various modes of MoS <sub>2</sub> functionalization with small molecules. These are (a) Covalent bonding, (b) coordination, and (c) Ligand conjugation <sup>22</sup>
Figure 6. STM images of DBT bound to the corner site of MoS <sub>2</sub> at different temperatures with edge sites (indicated by white arrows) remaining vacant (a, b) and schematic representation showing possible interaction only at the corner sites STM of adsorbed (left) and covalently modified (right) nanoflake (d). <sup>19</sup>
Figure 7 (A) Structural models illustrating ligand conjugation of chemically exfoliated MoS <sub>2</sub> sheets. (a) ζ-potential, (b) FT-IR spectra focused upon the thiol peak, (c) FT-IR spectra showing all peaks <sup>22</sup> 10
Figure 8. Comparison between (a) schematic of proposed "chemisorption" of thiol groups and (b) reduction of thiolated ligand and physisorption of the resulting disulfide. In (a) the chemisorbed ligand is pictorially proposed to slot into a sulfur defect via the sulfur atom of the thiol group, which then connects to the spacer group and a functional group at the end of the ligand <sup>24</sup> . In (b) an alternative reaction is proposed, in which two equivalents of a thiolated ligand (with any organic group R) converts into a disulfide product through interaction with the MoS <sub>2</sub> , with the R-groups remaining undisturbed <sup>21</sup>
Figure 9. Common groups discussed for the covalent functionalization (a) and coordination (b) of MoS <sub>2</sub> . Covalent functionalization has been primarily reported for iodo-organic compounds or diazonium salts, whereas

coordination has been reported only for structures with aromatic or ring structures, or which are capable of coordination through chelation of a metal acetate salt of nickel, copper, or zinc. <sup>22</sup>
Figure 10. Functional groups as described in the literature for Ligand Conjugation of (a) chemically exfoliated 1T-Mo <sub>2</sub> , and (b) 2H- MoS <sub>2</sub> . <sup>22</sup>
Figure 11. XPS spectra for v- MoS <sub>2</sub> , MEA- MoS <sub>2</sub> , and FDT- MoS <sub>2</sub> after the doping process: (a) C 1s; (b) N 1s; along with carrier density for both MEA and FDT on doped and annealed samples as compared to the original v-MoS <sub>2</sub> . Changes in PL are shown in (d-e) where (d) shows the n-doping phenomena after treatment with MEA, and (e) shows the p-doping phenomena resulting from treatment with FDT. <sup>24</sup>
Figure 12. Chemical Vapor Deposition precursor locations and set up within quartz tube. Sulfur powder is placed upstream in the outer quartz tube, while an inner quartz tube is placed downstream inside of the larger quartz tube. The inner tube contains two wafers of Si/SiO <sub>2</sub> with the silica side facing inwards. The WO <sub>3</sub> powder is placed between the silica wafers. Argon gas flows through the outer tube, carrying sulfur powder to the silica sandwich in the inner tube where it reacts with the WO <sub>3</sub> powder to form monolayer WS <sub>2</sub> 22
Figure 13. Synthesized monolayers and multilayers of WS <sub>2</sub> triangular islands characterized by (a) scanning electron microscopy (SEM), (b) Optical microscopy (OM), and (c) Fluorescence microscopy (FM). A pair of monolayer triangular regions of interest are outlined in red
Figure 14. (a) Schematic for full bubbler system for exposing substrate supported thin-layered material to aerosolized 2-mercaptoethanethiol is shown, along with (b) a photograph of the bubbler set up and (c) the molecular structure of the thiolated ligand used for treatment: 2-mercaptoethanethiol
Figure 15. Full Raman spectra, taken at 534 nm, of the WS <sub>2</sub> triangle before and after functionalization. An insert of the LA mode after functionalization highlights the region of interest, for which the spectra are presented
Figure 16. Curve-fitted spectra (a) before and (b) after treatment with 2-MEA. The spectra in (c) shows the change in the LA mode, and the emergent defect mode before and after treatment
Figure 17 . Curve-fitted spectra (a) before and (b) after treatment with 2-MEA. The spectra (c) shows the changes and overlap of the 2LA mode, the E2g mode, and the emergent defect mode before and after treatment
Figure 18. Raman mapping of the entire thin WS <sub>2</sub> triangle before (a and c) and after (b and d) treatment. Before treatment, both the intensity of the LA and

2LA mappings are uniform throughout the triangular monolayer, however after treatment an anisotropy in the mapping emerges through a loss of intensity centered at the lower right edge	.29
Figure 19. Raman mapping of the (a) A1g mode and the (b) peak width of the convoluted 2LA and E2g modes over a triangular island of monolayer tungsten disulfide,	.30
Figure 20. (a) Table of Fragment formulae and corresponding expected type of signature with (b) the molecular formula of 2-Mercaptoethaneamine and (c) the disulfide product with cleavage points a-c denoted	.34
Figure 21. Mass spectra focused on peaks of interest, particularly in the regions corresponding to the molecular weight of (a) 2-mercaptoethanamine, (b) the disulfide reaction product, and (c) a fragment of the disulfide reduction product. In all three spectra, the red upper line corresponds to spectra collected from post-treatment tungsten disulfide, and the grey line corresponds to the pristine, untreated tungsten disulfide	. 36
Figure 22. Mass spectra focused on peaks of interest, particularly in the regions corresponding to the molecular weight of (a) 2-mercaptoethanamine and a deprotonated benzene fragment, where the red upper line corresponds to spectra collected from post-treatment tungsten disulfide, and the grey line corresponds to the pristine, untreated tungsten disulfide. The spectra (b) corresponds to the net counts for the same range, and the theoretical mass isotope distributions are shown in (c) for 2-mercaptoethanamine and (d) for the deprotonated benzene fragment.	37
Figure 23. Mass spectra focused on peaks of interest, particularly in the regions corresponding to the molecular weight of (a) the disulfide reduction product of 2-mercaptoethanamine and a corresponding protonated fragment, where the red upper line corresponds to spectra collected from post-treatment tungsten disulfide, and the grey line corresponds to the pristine, untreated tungsten disulfide. The spectra (b) corresponds to the net counts for the same range, and the theoretical mass isotope distributions are shown in (c) the disulfide product of 2-mercaptoethanamine and (d) the protonated disulfide structure.	. 38
Figure 24. Mass spectra focused on peaks of interest, particularly in the regions corresponding to the molecular weight of (a) a fragment of the disulfide reduction product of 2-mercaptoethanamine, where the red upper line corresponds to spectra collected from post-treatment tungsten disulfide, and the grey line corresponds to the pristine, untreated tungsten disulfide. The spectra (b) corresponds to the net counts for the same range, and the	

spectra (b) corresponds to the net counts for the same range, and the theoretical mass isotope distribution is shown in (c) the disulfide product of

2-mercaptoethanamine. The point of cleavage is indicated in the structure shown in (d)	39
Figure 25. (a) AFM before functionalization of triangular region of interest, and (b) AFM using peakforce microscopy on the same triangle after functionalization	41
Figure 26. (a) Height, (b) Adhesion, (c) peak force error, and (d) deformation for tungsten disulfide after functionalization triangle using peak force microscopy	42
Figure 27 a. SEM image of full WS <sub>2</sub> sample, scale bar 20 um; b. higher resolution image of WS <sub>2</sub> with triangular features highlighted; c. region of AFM mapping with two features; d. AFM region with three features	14
Figure 28. a. 3D mapping of three triangular "hill" features; b. placement of three height profiles; c. graph of height profiles; d. measurements of three AFM features	45
Figure 29 a. Electron image of thicker WS <sub>2</sub> sample, b. sulfur series with inhomogeneity, c, Si series with minor inhomogeneity, d. tungsten series with little to no visible inhomogeneity present, and e. oxygen series with inhomogeneity via an absence of signal.	46
Figure 30. a. TEM image of $WS_2$ grain, b. TEM of large triangle, scale bar 2 $\mu$ m; c. Photoluminescence image of $WS_2$ on TEM grid before treatment, scale bar 100 $\mu$ m	17
Figure 31. Schematic for new two-input treatment system. One input will control the flow of argon through the bubbler of the thiolated organic material while a second controls an independent input for argon to permit greater control of the concentration of the ligand during treatment without compromising the flow rate for exposure	54
Figure 32 Schematic of selectively thiolated lateral heterostructure. The lateral heterostructure follows a core-shell structure such that the inner core of $MoS_2$ is surrounded by an outer layer of $WS_2$ . The boundary of these two regions is highlighted in red to illustrate the enhanced PL at this interface. Thiolated ligands are placed at various high defect-density regions such as the interface and edges of the lateral heterostructure, illustrating regions where selective adsorption of the ligands may occur.	56

## LIST OF TABLES

Table	1:	Table of e	experimental	design, ir	ndicating	number of	sample	s per trea	tment	
	p	resence or	absence on s	ilica eithe	er with or	without to	ungsten	disulfide		.31

Table 2: Concentration of elements detected during XPS for samples with and without
treatment, and silica controls samples. Relative ratio of sulfur to tungsten, residual
sulfur quantity and percentage of sulfur relative to percentage of tungsten
disulfide were also calcuated
Table 3: Table of Fragment formulae and corresponding expected type of signature (in
Figure 20a)
Table 4: Table of measurements of three AFM features (in Figure 28d)

#### ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my thesis advisor Dr. Mauricio Terrones for his continued support of this work. A special thanks to various members of the Terrones lab for their support and many discussions, and in particular to Ethan Kahn, Tiyanyi Zhang, and Dr. Kazunori Fujisawa for contributing to this work. Thanks also to Dr. Archi Dasgupta, Dr. Chanjing Zhang, and Tomotaroh Granzier-Nakajima for their help and support during the completion of this work. Finally, I must express my greatest appreciation to my parents, my brothers, and my dearest friends for providing me with unfailing support and continuous encouragement throughout my years of study. This accomplishment could not be possible without them. Thank you.

## **Chapter 1 Introduction**

#### **1.1 Transition Metal Dichalcogenides**

Thin layer transition metal dichalcogenides (TMDs) are of interest to the nanomaterials community because they can be semiconducting quasi-two-dimensional materials with potential applications as sensors and nanoelectronic devices. Most of the current research has been on the growth, characterization, and development of applications for single layers of these transition metal dichalcogenides (TMDs), because many of these materials' optoelectronic properties are more accessible in the mono-layer form<sup>1</sup>. While thin-layer semiconducting TMDs can be produced through a number of different growth methods, a common technique is chemical vapor deposition (CVD)<sup>2</sup>. For tungsten disulfide (WS<sub>2</sub>), the CVD growth method is particularly advantageous because the resulting samples are primarily in the 1H or the 2H phase as shown in figure 1, which is the semiconducting



Figure 1. Structural poly-types of pristine TMD layers. Chalcogen atoms are shown in yellow, and transition metal atoms are shown in blue. (a) The 1H phase, (b) the1T phase, (c) the distorted 1T, or1T' phase, (d) the 2H phase, (e) the 3R phase .<sup>4</sup>

phase of WS<sub>2</sub>. Other methods of synthesizing thin-layered samples, such as lithium intercalation, frequently result in the metallic 1T or 1T' phase of TMDs due to the interactions with the processing solution and require additional processing or annealing to produce the semiconducting phase<sup>3</sup>. These phases are also depicted in figure 1, as well as the 3R phase<sup>4</sup>.

### **1.2 Defects in TMDs**

## 1.2.1 Types of Defects

A variety of structural defects with different dimensionalities can also be introduced into TMDs. Of particular interest are atomic vacancies and topological defects, such as grain boundaries and exposed edges (see figure 2)<sup>5</sup>; these can serve as



Figure 2. Categorization of defects in two-dimensional TMDs by defect dimensionalities. TMD defects are classified by scale spanning (a) zero-dimensional, (b) one-dimensional, and (c) two-dimensional in structures. <sup>5</sup>

favorable active sites for the absorption of molecules, functional groups, and nanostructures, thus enabling various types of chemical and physical interactions. Other, larger scale defects such as in-plane grains, rippling, stacking and folding, which frequently occur and are dependent on higher-scale processing methods<sup>5</sup>, may also benefit from functionalization or interaction with other molecules or materials.

Regardless of the specific growth process, is important to consider the condition and quality of the resulting TMD. Given that most monolayer TMDs, such as tungsten disulfide, are only three atoms thick, any defects in the material can result in distortions of the crystal lattice and can greatly affect the desired optoelectronic properties under



Figure 3 Atomic-resolution annular dark field (ADF) images showing different types of vacancy and vacancy complexes in  $MoS_2$  monolayers. These zero-dimensional point defects involve single or multiple sulfur vacancies, or sulfur vacancies conjugated with a molybdenum atom or molybdenum vacancy.<sup>6</sup>

consideration. As shown in figure 3, there are several possible zeroth order point defects in our example TMD, MoS<sub>2</sub>, which illustrates the point for WS<sub>2</sub> as well<sup>6</sup>. These include: single sulfur vacancies (VS), double sulfur vacancies (V<sub>S2</sub>), a vacancy of a Mo atom and a triad of its bonded S within one plane (V<sub>MoS3</sub>), a vacancy of a Mo atom and all six of its nearest neighbors (V<sub>MoS6</sub>), an anti-site, with Mo occupying a V<sub>S2</sub> (MoS<sub>2</sub>), and a pair of S atoms occupying a Mo position (S2<sub>Mo</sub>). The absence of V<sub>Mo</sub> is expected due to its tendency to complex with sulfur vacancies. This high availability of the S vacancies would permit the presence of foreign atoms, either via adatom adsorption<sup>7</sup>, intercalation<sup>9,10</sup>, or through physi- and chemi-sorption of larger molecules onto the surface of the TMD<sup>10-12</sup>. Other defects of interest for this study include sulfur line vacancies, grain boundaries, and edges, which can still include an absence of sulfur in the crystal lattice<sup>5</sup>.

Many defects can be difficult and time consuming to find and quantify, and some methods may limit the optimal use of the material. Grain boundaries in particular can be easier to observe due nature of developing from the merging of two or more randomly



Figure 4. Grain boundaries in the 2D WS<sub>2</sub>, grown by CVD, are preferentially oxidized by controlled heating in air<sup>14</sup>.

oriented crystalline regions, however, they are structurally problematic because they serve as a point of degradation and have been observed to modulate the in-plane electrical conductivity<sup>13</sup>. Nevertheless, they are also more energetically active locations on the surface and therefore important for potential applications such as catalysis. To this end, a facile method of locating them would be useful. One such study makes such a priority by looking at grain boundaries in WS<sub>2</sub> for both polycrystalline films and CVD grown triangles. As shown in figure 4, it was noted that these boundaries could be preferentially oxidized by controlled heating in air, thus allowing for the removal of material near the boundaries and, in the case of CVD WS<sub>2</sub>, leaving isolated domains of highly crystalline material<sup>14</sup>. While method may be beneficial for testing representative samples of a large batch, however, this is a destructive process, and by removing the high energy defect regions, the opportunity to take advantage of the defect for further applications is also lost. Thus, the use of ligands which adsorb specifically onto these grain boundaries or other similar defects may be more useful in the long term, and this is one problem which will be addressed in this work.

#### **1.2.2 The Opportunities to Functionalize TMDs**

The commonly-used techniques for 2D semiconducting TMD synthesis and the opportunities of functionalization enabled by structural defects and different morphologies in TMDs can generally be categorized into two types of approaches: top-down and bottom-up<sup>15</sup>. Top-down approaches consist of the well-known scotch tape-based mechanical exfoliation, and chemical exfoliation or solvent-based processing

methods in which the bulk crystals can be thinned down to mono-layers in high yields<sup>16</sup>. Bottom-up approaches such as powder vaporization, chemical vapor deposition (CVD), and powder vapor deposition, have been widely used for TMD synthesis, which is a relatively scalable method for synthesizing monolayer TMDs with a high degree of crystallinity. For instance, by heating up the transition metal precursor inside a hightemperature furnace and permitting the simultaneous sulfurization/selenization of the metal with carrier gas flow, thin layers of TMDs can be deposited on a substrate placed downstream of the precursors. Additionally, colloidal synthesis and solution processing, is yet another important method for TMDs nanostructures with engineered morphology<sup>17</sup>. Through colloidal processing, high-surface area structures such as nanoflowers can be obtained, which make an ideal platform for chemical functionalization due to advantageous structural features such as exposed edges and decoupled layers<sup>17</sup>.

Sulfur vacancies are also useful specifically for ligand conjugation with thiolated organic adsorbents. As shown in figure 7, defects due to sulfur vacancies are present on both sides of the monolayer because this example involves exfoliated flakes of  $MoS_2$  in suspension<sup>10</sup>. Due to this, the thiolated ligands have free access to functionalize the TMD from both sides by conjugating the sulfur from the thiol group in the ligand with the vacancy. Similar other reports also used thiolated ligands and the presence of sulfur vacancies to functionalize TMDs, predominantly  $MoS_2^{10-12}$ .

#### 1.3 Towards functionalization and thiol adsorption on TMDs

Due to the highly interdisciplinary nature of the field, several works have studied a great variety of chemical and physical interactions that can be termed 'functionalization', 'modification', and 'conjugation'<sup>18</sup>. To pin a working definition, this introduction will broadly define functionalization as the manipulation of the TMD by chemisorption, physisorption, and electrostatic forces of a ligand which has been applied, attached, and/or interacts with the surface of the 2D material.

#### 1.3.1 Covalent functionalization and Coordination of thiolated ligands

A variety of terms cover surface-ligand interactions, in which small, usually thiolterminating ligand strongly bond to some defect on the surface, usually a sulfur-vacancy. These can be categorized as covalent, coordination, or ligand conjugation as described in figure 5. Reports of covalent functionalization include the work describing the covalent functionalization of chemically exfoliated 1T- MoS<sub>2</sub>, 1T- WS<sub>2</sub>, and 1T-MoSe<sub>2</sub> nanosheets by reacting them with organoiodides or diazonium salts<sup>8</sup>. Methods employing chemically exfoliated 1T- MoS<sub>2</sub> have provided the only routes to covalently functionalized TMDs to date. In the work involving organoiodides, XPS analysis indicated the absence of iodine atoms, suggesting functionalization through nucleophilic attack by the chemically exfoliated 1T- MoS<sub>2</sub> had occurred. XPS also confirmed the occurrence of nitrogen and carbon atoms on the surface, as well as the presence of new S-atoms, indicating the probable development of a new C-S bond.

While the first reports demonstrating chemisorption directly have strongly suggested the presence of edge- and corner-dominated adhesion<sup>19</sup>, other studies focus on the behavior on the basal plane<sup>20</sup>, where other competitive reactions may also occur



Figure 5.Graphical representations of various modes of  $MoS_2$  functionalization with small molecules. These are (a) Covalent bonding, (b) coordination, and (c) Ligand conjugation <sup>22</sup>

involving physisorption and other weaker interactions<sup>21</sup>, leading to a more complex association between the ligand(s) and the TMD surface.

Specifically, in the case of the first direct evidence of coordination between an organic ligand and a TMD, it is noted that the absorption of the ligand, dibenzothiophene (DBT), was observed on single-layer MoS<sub>2</sub> nanoclusters via scanning tunneling microscopy (STM) at the corner defects, as opposed to edge or basal defects<sup>19</sup>. This coordination of DBT should be contrasted with other reports of 'chemisorption' such as the similarly sized, thiol-bearing ligand, thionine, which was applied in sufficient quantities to MoS<sub>2</sub> during the sonication (with subsequent gradient centrifugation), in order to permit the expected subsequent organometallic complex to detect double-stranded DNA<sup>23</sup>. As shown in figure 6, the depicted work indicates that the edge-based adsorption was limited only by the availability of the defect regions, and speculates that a higher defect density at the edge sites might lead to higher efficacy unless otherwise capped by the degradation of the material or the steric hindrance of ligand-ligand interaction<sup>19</sup>.



Figure 6. STM images of DBT bound to the corner site of  $MoS_2$  at different temperatures with edge sites (indicated by white arrows) remaining vacant (a, b) and schematic representation showing possible interaction only at the corner sites STM of adsorbed (left) and covalently modified (right) nanoflake (d).<sup>19</sup>

### **1.3.2 Ligand Conjugation**

Two predominant mechanisms compete in the preexisting literature to describe the nature of "ligand conjugation". This type of ligand-surface interaction was first reported by Dravid and co-workers<sup>22</sup>. They reacted chemically exfoliated 1T- MoS<sub>2</sub> with bifunctional poly(ethylene glycol) (PEG) molecules, and observed a change of surface properties via large changes in the zeta potential of these functionalized materials. These results were supported by XPS analysis, which demonstrated the presence of carbon and oxygen atoms on the surface of these materials, thus indicating the incidence of polyether functional groups on the surface of the materials. FT-IR further suggested that thiol groups had reacted with the surface, as it was observed that the loss of the stretch at v S– H at 2563 cm –1 occurred after functionalization. While the disappearance of the thiol functionality would indicate a reaction with the ce-1T-MoS 2, this observation was rather vaguely described as the thiol being "buried" within the ce-1T-MoS<sub>2</sub> surface. Thus, the authors defined this type of functionalization as "ligand conjugation" with the organic



Figure 7 (A) Structural models illustrating ligand conjugation of chemically exfoliated  $MoS_2$  sheets. (a)  $\zeta$ -potential, (b) FT-IR spectra focused upon the thiol peak, (c) FT-IR spectra showing all peaks<sup>22</sup>

thiol, though the exact nature of the thiol-to-  $MoS_2$  interaction is left completely ambiguous. As shown in figure 7, the functionalization is described pictographically as a coordination between the thiol ligands and Molybdenum atoms in the chemically exfoliated 1T-  $MoS_2$  at S-vacancies, thus yielding a "ligand coordination" functionalization. However, little experimental evidence supports this claim. Other papers go on to use the "ligand conjugation" terminology to describe a variety of mechanisms with a large range of organic thiols on the surface,<sup>24</sup> as shown in figure 8.

Alternatively, it has been suggested that the thiol functionality does not fill Svacancies, but instead becomes converted to a disulfide that remains physisorbed on the MoS<sub>2</sub> surface<sup>21</sup>. Instead, the functionalization of 2H- MoS<sub>2</sub> results from the reduction of the thiolated ligand on the surface of the TMD, and the resulting disulfide is physisorbed on the surface. In order to investigate the functionalization by thiolated ligands, liquid exfoliated 2H- MoS<sub>2</sub> dispersed in isopropanol was treated with cysteine. These authors noted through UV-Visible spectroscopy and Raman Spectroscopy that a slightly modified 2H- MoS<sub>2</sub> remained<sup>21</sup>, unlike previous work described for covalent functionalization, which yields 1T- MoS<sub>2</sub>. Diffuse reflectance infrared Fourier transform (DRIFT) spectra also confirm that the material remains in the 2H phase after functionalization; although some changes are noted for certain notable peaks, the cause of this redshift was not explicitly described here. High-resolution X-ray photoelectron spectroscopy (XPS) analysis was also valuable to distinguish between the 2H- and 1T-phase; however, it was also useful for investigating surface functionalization of the 2D system. This comparison was achieved by the use of the molybdenum 3d core level spectra and sulfur 2p core level

spectra of Cysteine conjugated 2H- MoS<sub>2</sub> with the pristine 2H- MoS<sub>2</sub>. This work reported the XPS spectrum of cysteine exhibiting a single doublet of S 2p peaks with the S 2p3/2 binding energy at 163.5 eV, unlike the peak fitting of the S 2p spectrum of Cys-2H-MoS<sub>2</sub>, which resulted in two doublets<sup>21</sup>. The first doublet with S 2p3/2 binding energy at 161.8 eV provided the largest contribution (68%) and could be compared to the S 2p3/2 peak of the pristine 2H- MoS<sub>2</sub>. The second, smaller doublet with S 2p3/2 binding energy at 163.3 eV was attributed to the surface cysteine entities. Furthermore, a small shift in the binding energy of 0.2 eV in this smaller doublet relative to the measurement for pure cysteine was explained by a chemical change to the adsorbant molecule. From these measurements, it was determined that the component with the higher binding energy represented 32% of the S-atoms on the sample surface, indicating an equivalent functionalization which was confirmed using thermogravimetric (TGA) analysis<sup>21</sup>.



Figure 8. Comparison between (a) schematic of proposed "chemisorption" of thiol groups and (b) reduction of thiolated ligand and physisorption of the resulting disulfide. In (a) the chemisorbed ligand is pictorially proposed to slot into a sulfur defect via the sulfur atom of the thiol group, which then connects to the spacer group and a functional group at the end of the ligand<sup>24</sup>. In (b) an alternative reaction is proposed, in which two equivalents of a thiolated ligand (with any organic group R) converts into a disulfide product through interaction with the  $MoS_2$ , with the R-groups remaining undisturbed<sup>21</sup>.

#### 1.3.2 Ligand Alteration and Changes in Functional Groups or Moieties

A variety of effects and types of reactions occur as a result of the ligand used. Covalent functionalization, as shown in figure 9, utilizes chemically exfoliated 1T- MoS<sub>2</sub>. The most common types of covalent functionalization on MoS<sub>2</sub> occur through the application of organic iodides or diazonium salts. Unlike covalent functionalization, the coordination of organic ligands occurs on 2H-MoS<sub>2</sub>, and employs either larger aromatic rings with sulfur atoms incorporated in the ring structure, or use of a metal acetate salt. These can be coordinated to molybdenum atoms using the sulfur atom within the ring, but have only been observed in size-limited structures to date.

## Covalent Functionalization - ce-1T-MoS<sub>2</sub>



iodoacetamide

а

iodomethane



4-bromo- and 4-methoxyphenyl diazonium tetrafluoroborate

## Coordination to Mo- or by S-atoms - 2H-MoS<sub>2</sub>



Figure 9. Common groups discussed for the covalent functionalization (a) and coordination (b) of  $MoS_2$ . Covalent functionalization has been primarily reported for iodo-organic compounds or diazonium salts, whereas coordination has been reported only for structures with aromatic or ring structures, or which are capable of coordination through chelation of a metal acetate salt of nickel, copper, or zinc.<sup>22</sup>

Ligand conjugation, as an umbrella term, has been reported both on chemically exfoliated 1T-MoS<sub>2</sub> and on 2H-MoS<sub>2</sub>. In most instances, there are insufficient reports indicating if the majority are a reflection of covalent and/or coordination functionalization, or if these examples may instead follow the scheme 2 reaction mechanism involving physisorption of the disulfide reduction product on the surface of MoS<sub>2</sub>. For chemically exfoliated 1T- MoS<sub>2</sub>, several pegylated alkane thiols have been



Figure 10. Functional groups as described in the literature for Ligand Conjugation of (a) chemically exfoliated  $1T-Mo_2$ , and (b)  $2H-MoS_2$ .<sup>22</sup>

reported and can be seen in figure 10; with many organic ligands baring one or two thiol functional groups in addition to amine, hydroxide, or carboxyl groups<sup>10-12,20,22-24</sup>. An example of pegylated lipoic acid has also been reported, employing the disulfide bearing five-membered ring instead of a thiol group<sup>25</sup>. Ligand conjugation on 2H- MoS<sub>2</sub> has been described using similar organic ligands. Usually these bear a thiol group, but additionally are reported to contain alkanes of various lengths, as well as amines, carboxyl, phenol, and benzyl groups<sup>22, 26, 27</sup>. In one case, an organic ligand ended in trimethoxysilan<sup>28</sup>.

Most of these examples of ligand conjugation did not directly compare the effect of changing the terminating moiety; however, one study compared the effects of an amine bearing compound –mercaptoethaneamide (MEA) – with a multi-fluorine bearing compound – 1H,1H,2H,2H-perfluorodecanethiol (FDT) <sup>24</sup>. As demonstrated in figure 11, these ligands were chosen to explore the effect of charge doping that the change in moiety can provide. MEA was selected because the amine group was anticipated to be a p-doping source, due to the presence of the lone electron pairs for donation to the MoS<sub>2</sub>.



Figure 11. XPS spectra for v- MoS<sub>2</sub>, MEA- MoS<sub>2</sub>, and FDT- MoS<sub>2</sub> after the doping process: (a) C 1s; (b) N 1s; along with carrier density for both MEA and FDT on doped and annealed samples as compared to the original v- MoS<sub>2</sub>. Changes in PL are shown in (d-e) where (d) shows the n-doping phenomena after treatment with MEA, and (e) shows the p-doping phenomena resulting from treatment with FDT. <sup>24</sup>

On the other hand, the F-containing group, FDT, was used as an n-doping source as it was expected that the highly electronegative fluorine would withdraw electrons from the surface. As shown in figure 11, the results of these doping phenomena are characterized using XPS, photoluminescence (PL), and changes in carrier density as measured by FET devices. As shown in the C 1s XPS spectra for v- MoS<sub>2</sub>, MEA- MoS<sub>2</sub>, and FDT- MoS<sub>2</sub> before and after the doping process, the emergence of C-N peaks and C-F peaks indicate the presence of the ligand after application<sup>24</sup>. The emergence and absence of both the N 1s peak and N-H is shown in figure 10b beside the Mo Sp1/2 peak, which is shown in all three. It is also important to note that the MEA bearing, n-doping phenomena shows and improved charge carrier density, whereas the p-doping FDT shows a loss after doping, but recovers most of the loss after annealing. Finally, in figures 10d and 10e, the changes in photoluminescence are well explained by the n- and p-doping ligands respectively<sup>24</sup>. However, while the work reports the surface interaction phenomena as chemisorption, (see fig 7a) <sup>24</sup>, the justification for the adsorption mechanism is not clear.

#### **1.4 Experimental Design**

It is the aim of this work to elucidate the mechanism of ligand conjugation of thiol-bearing organic ligands on TMD monolayers. To this end, WS<sub>2</sub>, which is a TMD of comparable properties to MoS<sub>2</sub>, was employed; the ligand mercaptoethaneamide (MEA or 2-MEA) was also enlisted as it has a perceptible improvement in carrier density, which allows an additional characterization via several methods in order to determine the changes on the surface. Characterization include Optical Microscopy, Fluorescence Microscopy, Raman Spectroscopy, Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Thus, this method of surface functionalization of WS<sub>2</sub> provides an ideal platform in which the interaction between the ligand and the 2D-TMDs may be probed to determine the type of reaction which occurs on the surface.

## 1.5 Bibliography

- Wang, H.; Yuan, H.; Sae Hong, S.; Li, Y.; Cui, Y. Physical and Chemical Tuning of Two-Dimensional Transition Metal Dichalcogenides. *Chem. Soc. Rev.* 2015, 44, 2664–2680.
- Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* 2013, *5*, 263–275.
- 3. Py, M. A. & Haering, R. R. Structural destabilization induced by lithium intercalation in MoS<sub>2</sub> and related compounds. Can. J. Phys. **1983**, *61*, 76–84
- 4. Voiry, D.; Mohite, A.; Chhowalla, M. Phase Engineering of Transition Metal Dichalcogenides. *Chem. Soc. Rev.* **2015**, *44*, 2702–2712.
- Lin, Z.; Carvalho, B. R.; Kahn, E.; Lv, R.; Rao, R.; Terrones, H.; Pimenta, M. A.; Terrones, M. Defect Engineering of Two-Dimensional Transition Metal Dichalcogenides. 2D Mater. 2016, 3, 22002.
- Zhou, W.; Zou, X. L.; Najmaei, S.; Liu, Z.; Shi, Y. M.; Kong, J.; Lou, J.;
   Ajayan, P. M.; Yakobson, B. I.; Idrobo, J. C. Intrinsic Structural Defects in Monolayer Molybdenum Disulfide. Nano Lett. 2013, 13, 2615–2622
- Zhou, W.; Zou, X. L.; Najmaei, S.; Liu, Z.; Shi, Y. M.; Kong, J.; Lou, J.;
   Ajayan, P. M.; Yakobson, B. I.; Idrobo, J. C. Intrinsic Structural Defects in Monolayer Molybdenum Disulfide. Nano Lett. 2013, 13, 2615–2622
- Knirsch, K. C.; Berner, N. C.; Nerl, H. C.; Cucinotta, C. S.; Gholamvand, Z.; McEvoy, N.; Wang, Z.; Abramovic, I.; Vecera, P.; Halik, M.; *et al.* Basal-Plane Functionalization of Chemically Exfoliated Molybdenum Disulfide by Diazonium Salts. *ACS Nano* 2015, *9*, 6018–6030.
- Kiran, V.; Mukherjee, D.; Jenjeti, R. N.; Sampath, S. Active Guests in the MoS<sub>2</sub>/MoSe2 Host Lattice: Efficient Hydrogen Evolution Using Few-Layer Alloys of MoS(2(1-x))Se(2x). *Nanoscale* 2014, 6, 12856–12863.
- Cho, K.; Min, M.; Kim, T.-Y.; Jeong, H.; Pak, J.; Kim, J.; Jang, J.; Yun, S. J.;
   Lee, Y. H.; Hong, W.; *et al.* Electrical and Optical Characterization of MoS<sub>2</sub>

with Sulfur Vacancy Passivation by Treatment with Alkanethiol Molecules. *ACS Nano* **2015**, 8044–8053.

- Chou, S. S.; De, M.; Kim, J.; Byun, S.; Dykstra, C.; Yu, J.; Huang, J.; Dravid,
   V. P. Ligand Conjugation of Chemically Exfoliated MoS<sub>2</sub>. *J. Am. Chem. Soc.* 2013, *135*, 4584–4587.
- Kim, J. S.; Yoo, H. W.; Choi, H. O.; Jung, H. T. Tunable Volatile Organic Compounds Sensor by Using Thiolated Ligand Conjugation on MoS<sub>2</sub>. *Nano Lett.* 2014, 14, 5941–5947.
- van der Zande, A.M.; Huang, P. Y.; Chenet, D. A.; Berkelbach, T. C.; You, Y.; Lee, G. H.; Heinz, TF; Reichman, D.R.; Muller, D. A.; and Hone, J.C.; Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide; *Nat. Mater.* 2013, *12*, 554
- Rong, Y.; He, K.; Pacios, M.; Robertson, A. W.; Bhaskaran, H.; Warner, J. H. Controlled Preferential Oxidation of Grain Boundaries in Monolayer Tungsten Disulfide for Direct Optical Imaging. *ACS Nano* 2015, *9*, 3695–3703.
- Das, S., Robinson, J. A., Dubey, M., Terrones, H., & Terrones, M. (2015).
   Beyond Graphene: Progress in Novel Two-Dimensional Materials and van der Waals Solids. *Annual Review of Materials Research*, 45(1), 1–27. https://doi.org/10.1146/annurev-matsci-070214-021034
- Eda, G., Yamaguchi, H., Voiry, D., Fujita, T., Chen, M., & Chhowalla, M.
   (2011). Photoluminescence from chemically exfoliated MoS 2. *Nano Letters*, *11*(12), 5111–5116. https://doi.org/10.1021/nl201874w
- Sun, D., Feng, S., Terrones, M., & Schaak, R. E. (2015). Formation and interlayer decoupling of colloidal MoSe<sub>2</sub> nanoflowers. *Chemistry of Materials*, 27(8), 3167–3175. https://doi.org/10.1021/acs.chemmater.5b01129
- Presolski, S., & Pumera, M. (2016). Covalent functionalization of MoS2.
   *Materials Today*, 19(3), 140–145.
   https://doi.org/10.1016/j.mattod.2015.08.019
- 19. Tuxen, A., Kibsgaard, J., Gøbel, H., Lægsgaard, E., Topsøe, H., Lauritsen, J.V., & Besenbacher, F. (2010). Size threshold in the dibenzothiophene

adsorption on MoS2 nanoclusters. *ACS Nano*, *4*(8), 4677–4682. https://doi.org/10.1021/nn1011013

- Ding, Q., Czech, K. J., Zhao, Y., Zhai, J., Hamers, R. J., Wright, J. C., & Jin, S. (2017). Basal-Plane Ligand Functionalization on Semiconducting 2H-MoS
   Monolayers. ACS Applied Materials & Interfaces, acsami.7b01262.
- Chen, X., Berner, N. C., Backes, C., Duesberg, G. S., & McDonald, A. R. (2016). Functionalization of Two-Dimensional MoS2: On the Reaction between MoS2 and Organic Thiols. *Angewandte Chemie International Edition*, 55(19), 5803–5808. https://doi.org/10.1002/anie.201510219
- 22. Chen, X., McDonald, A. R. (2016). Functionalization of Two-Dimensional Transition-Metal Dichalcogenides. *Advanced Materials*, 28(27), 5738–5746.
- Wang, T., Zhu, R., Zhuo, J., Zhu, Z., Shao. Y., Li, M., (2014). Direct Detection of DNA below ppb Level Based on Thionin-Functionalized Layered MoS2 Electrochemical Sensors. *Analytical Chemistry*, 86 (24), 12064-12069
- Sim, D. M., Kim, M., Yim, S., Choi, M. J., Choi, J., Yoo, S., & Jung, Y. S. (2015). Controlled Doping of Vacancy-Containing Few-Layer MoS<sub>2</sub> via Highly Stable Thiol-Based Molecular Chemisorption. *ACS Nano*, 9(12), 12115–12123.
- Liu, T., Wang, C., Gu, X., Cheng, L., Shi, X., Feng, L., Sun, B., Lui, Z.,
   (2014) Drug delivery with PEGylated MoS2 nano-sheets for combined photothermal and chemotherapy of cancer., *Adv. Mater.* 2014, 26, 3433.
- Cheng, Z., He, B., Zhou, L.,(2015) A general one-step approach for *in* situ decoration of MoS<sub>2</sub> nanosheets with inorganic nanoparticles *J. Mater.* Chem. A 3, 1042.
- Liu, T., Shi,S., Liang, C., Shen, S., Cheng, L., Wang, C., Song, X., Goel, S., Barnhard, T. E., Cai, W., Liu, Z., (2015) Iron oxide decorated MoS2 nanosheets with double PEGylation for chelator-free radiolabeling and multimodal imaging guided photothermal therapy.*ACS Nano*, 9, 950.

Jiang, S.-D., Tang, G., Bai, Z.-M., Wang, Y.-Y., Hu, Y., Song, L., (2014)
Highly concentrated MoS<sub>2</sub> nanosheets in water achieved by thioglycolic acid as stabilizer and used as biomarkers *RSC Adv.* 4, 3253.

## Chapter 2

## **Functionalization of WS**<sub>2</sub>

## 2.1 Growth of WS<sub>2</sub>

The WS<sub>2</sub> growth for this project was carried out by chemical vapor deposition (CVD) inside a quartz tube. Approximately 10 mg of tungsten oxide (WO<sub>3</sub>) powder was sandwiched between two pieces of Si/SiO<sub>2</sub> wafers, where the 300 nm layer of silica faces the powder (Fig. 12). This "sandwich" was placed within a small inner quartz tube positioned inside of the larger quart tube, along with 400 mg of sulfur powder placed upstream directly inside of the outer tube, as shown in figure 12. Before growth, the quartz tube was flushed with Argon gas for 20 minutes at 300 sccm, and then reduced to 200 sccm when carrying out the growth process. WS<sub>2</sub> growth occurred through a two-step temperature program for the furnace, first ramping from room temperature to 500°C



Figure 12. Chemical Vapor Deposition precursor locations and set up within quartz tube. Sulfur powder is placed upstream in the outer quartz tube, while an inner quartz tube is placed downstream inside of the larger quartz tube. The inner tube contains two wafers of Si/SiO<sub>2</sub> with the silica side facing inwards. The WO<sub>3</sub> powder is placed between the silica wafers. Argon gas flows through the outer tube, carrying sulfur powder to the silica sandwich in the inner tube where it reacts with the WO<sub>3</sub> powder to form monolayer WS<sub>2</sub>.

in 15 minutes, and then immediately to 700°C in the following 15 minutes, where it is held for 15 minutes, before being allowed to cool naturally. The sulfur powder heating was also controlled via a heating belt, which ramped from room temperature to 70°C in 10 minutes, holding at 70°C for 15 minutes, and then heating up to 300°C for 5 minutes more, and holding for 10 minutes. After growth, samples of WS<sub>2</sub> were characterized initially with optical and fluorescence microscopy to determine if a sample is viable and consists of WS<sub>2</sub> monolayers. WS<sub>2</sub> monolayers demonstrated edge enhanced photoluminescence, as shown in figure 13. Viable samples for further treatment were also



SEM image of a pair of Monolayer WS<sub>2</sub> triangles



Optical image



Fluorescence

Figure 13. Synthesized monolayers and multilayers of WS<sub>2</sub> triangular islands characterized by (a) scanning electron microscopy (SEM), (b) Optical microscopy (OM), and (c) Fluorescence microscopy (FM). A pair of monolayer triangular regions of interest are outlined in red.

characterized in a variety of other methods for later comparison, including Raman spectroscopy, AFM, and SEM.

## 2.2 Functionalization of WS<sub>2</sub> Monolayers

These samples of thin-layered WS<sub>2</sub> were then treated using aerosolized 2mercaptoethanethiol through a bubbler-based setup in order to the improve selectivity and to better suit the CVD-grown WS<sub>2</sub> supported on a silica substrate, as shown in figure 14. A solution mixture of 2-mercaptoethanethiol and ethanol, the carrier solvent, was added to a bubbler up to a maximum saturation of 0.01g/ml of 2-mercaptoethanethiol in ethanol. This bubbler has a line of argon attached to a mass flow controller which has



Figure 14. (a) Schematic for full bubbler system for exposing substrate supported thin-layered material to aerosolized 2-mercaptoethanethiol is shown, along with (b) a photograph of the bubbler set up and (c) the molecular structure of the thiolated ligand used for treatment: 2-mercaptoethanethiol.

been tested for this solution between 15 sccm and 250 sccm through repeated trials, with a maximum upper limit determined at 150 sccm for producing viable samples. This bubbler was attached to a quartz tube, within which lies a silica-supported TMD sample resting on a quartz slide, centered at twelve centimeters from the end of the tube.

Unlike bulk grown and intercalated samples, or other similar top-down processed thin-layer TMDs, these WS<sub>2</sub> monolayer 'triangles' have the benefit of an underlying substrate, which act as a structural support. Immersion-and-rinse methods<sup>1-6</sup> described by other thiolated ligand functionalization procedures may not be appropriate for CVD grown samples due to the presence of the silica substrate, as only one face of the TMD is exposed. Furthermore, the bubbler system would permit further control and selectivity of functionalization through the solution concentration, the mass flow of gas, and exposure; whereas immersion methods are dependent on solution concentrations. Since a maximum flow rate of 150 sccm was determined for the bubbler set up, most of the samples were treated using this flow rate. However, several samples treated at 100 sccm also appeared to have been successfully functionalized, so further reduction of the flow rate may be explored to attain selectivity after a suitable efficiency has been fully determined.

#### 2.3 Characterization of WS<sub>2</sub> Monolayers

#### 2.3.1 Raman Spectroscopy Studies

Raman spectra of a single, unobstructed triangular monolayers of  $WS_2$  were taken before and after functionalization, and mappings of the LA and 2LA Raman modes were studided figure 15. Before functionalization, both modes demonstrated a fairly uniform intensity over the entire triangle except at the edges. However, after exposure with 2mercaptoethanethiol for 30 minutes with an argon flow rate at 150 sccm, there are notable differences in the mappings of both modes. The intensity of the 2LA and  $E_{2g}$  modes



Figure 15. Full Raman spectra, taken at 534 nm, of the WS<sub>2</sub> triangle before and after functionalization. An insert of the LA mode after functionalization highlights the region of interest, for which the spectra are presented.

decrease significantly from the top right edge, where it is the highest, to the bottom left corner, where it is the lowest.

By zooming in to the 150-200 cm<sup>-1</sup> region of the overlapping Raman spectra, changes in the LA mode can be clearly observed. Curve fittings of the selected, normalized region were performed to deconvolute the LA mode from a neighboring, overlapping defect peak. (fig. 16a and 16b). The defect peak centered at 190 cm<sup>-1</sup> (shown in red in 16a and 16b) corresponds with the peak at the same wavenumbers<sup>7</sup>; and this peak has a very similar intensity before and after treatment. However, there are changes observed in the LA mode. In Figure 16c, the LA mode is shown before and after functionalization, where approximately half the intensity (by height) is lost, and redshift of 12 cm<sup>-1</sup> occurs. As the LA mode has been associated to the presence of defects and it is related to the relative path length between defects in the crystalline lattice. Therefore, a



Figure 16. Curve-fitted spectra (a) before and (b) after treatment with 2-MEA. The spectra in (c) shows the change in the LA mode, and the emergent defect mode before and after treatment.

loss in the intensity may suggest that the some passivation, or improvement of the defect character has occurred. As the only change relates to the treatment of  $WS_2$  by the 2-MEA, it may indicate that some of the sulfur vacancies may have been electronically or structurally passivized by the presence of the organic treatment. The slight blue-shift of the peak may indicate an increase in the presence of charge carriers, which may have originated from the introduction of the thiolated ligand<sup>6</sup>.

This result may seem counter-intuitive if in the proposed circumstance of a direct bonding or strong electrostatic interaction with the surface should occur, as it would be expected that the amine group on the 2-MEA would lead to a withdrawal of charge from the WS<sub>2</sub>. However, under the occurrence that a possible reduction of the thiolated ligands



Figure 17 . Curve-fitted spectra (a) before and (b) after treatment with 2-MEA. The spectra (c) shows the changes and overlap of the 2LA mode, the E2g mode, and the emergent defect mode before and after treatment.

should lead to the production of a disulfide bond, it would be reasonable that the electron freed during the reduction may transfer to the surface.

Similarly, a focus on the to the 300 to 400 cm<sup>-1</sup> spectral region of the overlapping Raman spectra, changes in the 2LA and  $E_{2g}$  modes can be observed. Curve fittings of the selected, normalized region were done to deconvolute selection of peaks (fig. 17a and 17b). A defect peak, (shown in red in 17a and 17b shows a very similar intensity, and results from the linear combination of two defects peaks). In these two spectra, the 2LA mode and  $E_{2g}$  is shown before and after functionalization. From the curve fitting, an



Figure 18. Raman mapping of the entire thin  $WS_2$  triangle before (a and c) and after (b and d) treatment. Before treatment, both the intensity of the LA and 2LA mappings are uniform throughout the triangular monolayer, however after treatment an anisotropy in the mapping emerges through a loss of intensity centered at the lower right edge.

emergent mode arises along with the 2LA mode. The 2LA mode, the  $E_{2g}$  mode, and the emergent defect mode are shown in Fig 17c with overlapping spectra from before and after functionalization. It is shown that all three peaks decrease greatly in intensity, especially the 2LA mode, which is the double resonance of the LA mode. As the 2LA mode can rely on the presence of the LA defect mode, it may be a reflection of the changes in the total intensity and shift in energy which results in a significantly reduced resonance mode. Furthermore, the  $E_{2g}$  mode decreases greatly, and the band broadens, with a mild loss of area under the curve. The  $E_{2g}$  mode corresponds to in-plane motion, so the lower intensity and broadening of the peak after functionalization would reflect the demonstrated anisotropy over the entire triangular island, as presented in figure 18.

The mappings in figure 19 provide information on the  $A_{1g}$  mode (figure 19a), and the peak width of 2LA and  $E_{2g}$  modes. The  $A_{1g}$  band corresponds to out of plane motion.





After treatment : A<sub>1q</sub> Peak

After treatment: 2LA and  $E_{2g}$ peak width



The total intensity of the normalized spectra indicate that the total intensity before and after treatment does not significantly change the shape or size of the peak. A mapping of the region after treatment demonstrates that there is no anisotropy in the intensity of the peak over the entire triangle. However, there the mapping of the peak width over the convoluted 2LA and  $E_{2g}$  bands which demonstrate the anticipated anisotropy as previously discussed in the mappings in figure 18.

### 2.3.2 XPS Studies of Functionalized WS<sub>2</sub> Monolayers

In order to understand the elemental composition on the surface of the 2-MEA treated tungsten disulfide, X-ray photoelectric spectroscopy (XPS) was employed. Time-of-Flight Secondary Ion Mass Spectroscopy followed, as described in section 2.3.3. A series of samples and controls was created using the schematic shown in Table 1, with two silica samples, and two silica-supported WS<sub>2</sub> samples. One each of the silica and WS<sub>2</sub> was treated with 2-MEA while the remaining sample was left untreated as control for the presence of 2-MEA.

Number of Samples	Bare Silica Wafer	WS <sub>2</sub> present
Treatment (30 min)	1	1
No Treatment	1	2

Table 1: Table of experimental design, indicating number of samples per treatment presence or absence on silica either with or without tungsten disulfide

XPS was performed on these samples in order to determine the extent of change that occurred on the surface after exposure to 2-Mercaptoethaneamine. From the percentages shown in table 2, it is shown that using the tungsten 4f7/2 peak, the presence of  $WS_2$  can be confirmed for the samples labeled to contain  $WS_2$ . It was reported that nitrogen was detected at the surface for all the functionalized samples, both with  $WS_2$  and with the blank control silica, and was absent on the non-functionalized samples. However, on the silica control exposed to 2-MEA, the presence of sulfur on the surface was below the detection limit, unlike on the two samples with  $WS_2$  present. This is reasonable when compared to the relatively low percentage of nitrogen on the blank sample. The excess sulfur for these samples, and the control  $WS_2$  samples from CVD growth and from exfoliation are shown in table 2. Using the amount of tungsten disulfide, and the relative ratios of sulfur to tungsten, the residual sulfur, in excess of that expected for the crystalline structure of thin layered WS<sub>2</sub>, was calculated. The percentage of this excess sulfur relative to the amount of tungsten disulfide present in the measurement was then calculated. Although there are comparable amounts of residual sulfur on the surface for the two functionalize TMD samples, the control, non-treated  $WS_2$  had such a low quantity of excess sulfur as to be below the detection limit. Furthermore, the exfoliated sample of  $WS_2$  had a similar count of residual sulfur, but the relative percentage of residual sulfur on the surface was determined to be under five percent (at under 0.1% for  $WS_2$  and 4.6% for the exfoliated sample, from HQ graphene  $WS_2$ ), unlike the higher values given by the 2-MEA treated samples. The excess sulfur on the untreated and exfoliated sample can be mainly attributed to excess sulfur on the edges and as a minor ad-layer of sulfur atom left behind from the exfoliation process. Thus, the higher values

for the WS<sub>2</sub>-relative percentage of sulfur can be attributed solely to the exposure of the TMD samples to the aerosolized 2-MEA. These XPS experiments were performed using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al k $\alpha$  x-ray source (hv = 1,486.7 eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons (<5 eV) and argon ions. The binding energy axis was calibrated using sputter cleaned Cu foil (Cu  $2p_{3/2} = 932.7$  eV, Cu  $2p_{3/2} = 75.1$  eV). Peaks were charge referenced to CH<sub>x</sub> band in the carbon 1s spectra at 284.8 eV. Measurements were carried out at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3-6 nm (95% of the signal originated from this depth or shallower). Quantification was performed using instrumental relative sensitivity factors (RSFs) that account for the x-ray cross section and inelastic mean free path of the electrons.

Sample	с	N	o	s	Si	w	s/w	WS2	Residual S	% Residual S
WS2+CF (II)	14.20	1.80	46.50	7.30	27.50	2.70	2.70	2.40	2.50	34.25
WS2+CF (I)	8.90	1.40	51.00	3.70	33.90	1.10	3.40	1.00	1.70	45.95
Blank CF	5.70	0.10	59.60	-	34.50	-	-	-	-	-
Blank no CF	4.60	-	60.50	-	34.90	-	-	-	-	-
WS2	19.70	-	31.50	18.80	19.70	10.30	1.83	9.40	0.00	0.00
HQ Graphene WS2	10.30			60.80		29.00	2.10	29.00	2.80	4.61

Table 2: Concentration of elements detected during XPS for samples with and without treatment, and silica controls samples. Relative ratio of sulfur to tungsten, residual sulfur quantity and percentage of sulfur relative to percentage of tungsten disulfide were also calculated.

#### 2.3.3 ToF-SIMS Studies on Functionalized WS<sub>2</sub> Monolayers

To further understand the elemental composition on the surface of the 2-MEA treated WS<sub>2</sub>, Time-of-Flight Secondary-Ion Mass Spectroscopy (ToF-SIMS) was also employed, using the sample and control schematic in section 2.3.2 including two silica samples, and two silica-supported WS<sub>2</sub> samples. One each of the silica and WS<sub>2</sub> was treated with 2-MEA while the remaining sample was left untreated as control for the presence of 2-MEA.

An overview of the anticipated fragments' formulae and the corresponding structure and mechanism type is shown in Figure 20(a). The first three fragments correspond to the structure of 2-Mercaptoethanamine, shown in 20b, with a protonated and deprotonated fragment also listed. The next three fragments were based on the a

Fragments	Preceding Reaction Type
C <sub>2</sub> H <sub>6</sub> SN	Single Molecule Signature of C <sub>2</sub> H <sub>6</sub> SN
C <sub>2</sub> H <sub>5</sub> SN	Single Molecule Signature of C <sub>2</sub> H <sub>6</sub> SN
C <sub>2</sub> H <sub>7</sub> SN	Single Molecule Signature of C <sub>2</sub> H <sub>6</sub> SN
$C_4H_{12}S_2N_2$	Disulfide Reduction Product Signatures of $C_4H_{12}S_2N_2$
$C_4H_{11}S_2N_2$	Disulfide Reduction Product Signatures of $C_4H_{12}S_2N_2$
$C_4H_{13}S_2N_2$	Disulfide Reduction Product Signatures of $C_4H_{12}S_2N_2$
$C_3H_8S_2N$ (plus residual $CH_4N$ )	Reduction Product post-cleavage Signature – at cleavage point a
$C_2H_6S_2N$ (plus residual $C_2H_6N$ )	Reduction Product post-cleavage Signature – at cleavage point b
$C_4 H_{12} S_2 N$ (plus residual (NH_2)	Reduction Product post-cleavage Signature –at cleavage point c

Figure 20. (a) Table of Fragment formulae and corresponding expected type of signature with (b) the molecular formula of 2-Mercaptoethaneamine and (c) the disulfide product with cleavage points a-c denoted.

disulfide structure as shown on 20c, where the post-reaction disulfide product of 2-Mercaptoethanamine is listed along with the protonated or deprotonated fragment. The final three structures are the based on the disulfide product, but the three mostly likely points of cleavage are highlighted in 20c, and the larger fragment is listed in the table, along with the residual moiety that would be released during the mid-experiment cleavage. This cleavage was predicted to occur during data collection, when the surface is bombarded with Ga+ ions in order to facilitate collection of secondary ions. The smaller, residual moieties all have molecular weights which are very low and overlap with common volatile organic compounds and fragments commonly measured and used for calibration purposes, and thus were not considered. However, the larger of the postreaction cleavage fragments would be anticipated under the circumstances that the disulfide producing reduction occurred on the surface of the WS<sub>2</sub> monolayer.

Through the comparison of the treated and untreated samples, particular regions of interest on the collected mass spectra corresponding to the single molecule, the disulfide reaction product, and a selected post-cleavage fragment which was present after bombardment with the gallium cations for the generation of secondary ions. As shown in figure 21, the specific peaks of interest as listed in Figure 20 were narrowed down to the mass spectra are focused on these specific peaks of interest, particularly in the regions corresponding to the molecular weight of (21a) 2-mercaptoethanamine, (21b) the disulfide reaction product, and (21c) a fragment of the disulfide reduction product. In all three spectra, the red upper line corresponds to spectra collected from post-treatment tungsten disulfide, and the grey line corresponds to the pristine, untreated tungsten disulfide. It is clear that for mass region of 75-78 amu, the 2-MEA peak and protonated

peak are shown, in a region overlapping the a benzene deprotonated fragment, as shown in figure 22. Closer investigation into the theoretical mass isotopes distribution was necessary for these samples, as presented in figures 22 through 24.

A focus on the selected regions in Figure 11 was necessary for identifying the molecular structures of the present organic material. As shown in figure 12, mass spectra focused on peaks of interest, particularly in the regions corresponding to the molecular masses of 2-mercaptoethanamine and a deprotonated benzene fragment, as shown in figure 21a. For these spectra, the red upper line corresponds to spectra collected from post-treatment WS<sub>2</sub>, and the grey line corresponds to the pristine, untreated WS<sub>2</sub>. The



Figure 21. Mass spectra focused on peaks of interest, particularly in the regions corresponding to the molecular weight of (a) 2-mercaptoethanamine, (b) the disulfide reaction product, and (c) a fragment of the disulfide reduction product. In all three spectra, the red upper line corresponds to spectra collected from post-treatment tungsten disulfide, and the grey line corresponds to the pristine, untreated tungsten disulfide.

spectra in figure 21b corresponds to the net counts for the same range, indicating to total counts which are can be attributed to the presence of the organic molecule, by taking the difference in counts between the treated WS<sub>2</sub> sample and the control WS<sub>2</sub> sample. By using the theoretical mass isotope distributions as shown in figure 21c, for 2-mercaptoethanamine, and in figure 21d, for the deprotonated benzene fragment, it can be determined that the single molecule structure matched the peak at 76 amu. However, the presence of the deprotonated benzene fragment overshadows the expected protonated fragment of 2-MEA at 77 amu, and therefore the presence of single molecule structure is only indicated by the moderate intensity of the primary peak centered at 76 amu.



Figure 22. Mass spectra focused on peaks of interest, particularly in the regions corresponding to the molecular weight of (a) 2-mercaptoethanamine and a deprotonated benzene fragment, where the red upper line corresponds to spectra collected from post-treatment tungsten disulfide, and the grey line corresponds to the pristine, untreated tungsten disulfide. The spectra (b) corresponds to the net counts for the same range, and the theoretical mass isotope distributions are shown in (c) for 2-mercaptoethanamine and (d) for the deprotonated benzene fragment.

The investigation of the disulfide reaction product through ToF-SIMS initially provided spectra which demonstrated very low intensities in the regions of interest as shown in figure 22. A selected region of the mass spectra focused on peaks of interest, particularly in the region between 151 and 158 amu. This region corresponds to the molecular weight of the disulfide reduction product of 2-mercaptoethanamine and a corresponding protonated fragment as shown in figure 22a, where the red upper line corresponds to spectra collected from post-treatment WS<sub>2</sub>, and the grey line corresponds to the net counts for the same range, indicating to total counts that can be attributed to the presence of organic molecules, by taking the difference in counts between the treated WS<sub>2</sub> monolayer sample and the control WS<sub>2</sub> monolayer sample. The theoretical mass isotope



Figure 23. Mass spectra focused on peaks of interest, particularly in the regions corresponding to the molecular weight of (a) the disulfide reduction product of 2-mercaptoethanamine and a corresponding protonated fragment, where the red upper line corresponds to spectra collected from post-treatment tungsten disulfide, and the grey line corresponds to the pristine, untreated tungsten disulfide. The spectra (b) corresponds to the net counts for the same range, and the theoretical mass isotope distributions are shown in (c) the disulfide product of 2-mercaptoethanamine and (d) the protonated disulfide structure.

distributions of the disulfide product are shown in figure 22c, indicates the highest intensity for the most common isotope at 152 amu, whereas the theoretical mass isotope distribution for the protonated disulfide product was determined to be predominantly at 153 amu. By comparing these mass isotope distributions with the net spectra, it was concluded that while both peaks had low intensities, the peak at 153 amu had a higher intensity, corresponding to the protonated disulfide product. This was understood as a result of the expected positive charge on the surface due to the gallium cation, and the detector during the ToF-SIM experiment having an intended selectivity focused toward positive ions.



Figure 24. Mass spectra focused on peaks of interest, particularly in the regions corresponding to the molecular weight of (a) a fragment of the disulfide reduction product of 2mercaptoethanamine, where the red upper line corresponds to spectra collected from posttreatment tungsten disulfide, and the grey line corresponds to the pristine, untreated tungsten disulfide. The spectra (b) corresponds to the net counts for the same range, and the theoretical mass isotope distribution is shown in (c) the disulfide product of 2-mercaptoethanamine. The point of cleavage is indicated in the structure shown in (d)

Due to the very low count of the full disulfide structure of the possible reduction of 2-MEA, the mass spectra focused on the three locations where the structure could break were also investigated. Of the three possible regions (as listed in figure 24), the structure corresponding to option b, where the cleavage occurs between a sulfur from the disulfide bond, and sp<sup>3</sup> hybridized carbon bonded to it. The supporting mass spectra, as shown in figure 24, depicts the region between 107 and 112 amu. In this selected region of the mass spectra, the overlapped spectra in figure 24a corresponded to the molecular weight of the post-cleavage disulfide reduction product of 2-mercaptoethanamine where the red upper line corresponds to spectra collected from post-treatment WS<sub>2</sub>, and the grey line corresponds to the pristine, untreated tungsten disulfide. The spectra shown in figure 24b, corresponding to the net counts for the same range, indicate to total counts expected to be attributed to the presence of the post-cleavage organic fragments, by taking the difference in counts between the treated  $WS_2$  sample and the control  $WS_2$  sample. The theoretical mass isotope distribution for this fragment demonstrates that the peak of highest intensity is expected to occur at 108 amu, with is shown in figure 24c, thus matching the relative intensities shown in the net spectra from figure 24b. The point of cleavage is indicated in the structure shown in figure 24d, where the breakage occurs between one of the sulfur atoms in the disulfide bond and the carbon bonded to it. This result confirms the expectation that the new disulfide bond would have an increased electron density, thus lowering the density around the bond between the sulfur and the sp<sup>3</sup> carbon nearest to it.

#### 2.3.4 AFM Studies of Functionalized WS<sub>2</sub> Monolayers

The thinnest WS<sub>2</sub> appears to have only slightly increased the height on the corner where the loss of intensity was mostly strongly observed in the Raman mapping. No other region appeared to have this slight increase in height. The AFM from before the MEA treatment, as shown in grey-scale on the left of figure 25, has a maximum of 1.2 nm from the edge of the silica substrate observed from the height profile taken across the triangle. After treatment, the maximum increased the 3.0 nm, as shown in the Peakforce AFM data from the right side of figure 25. However, since the height is lower than the previously observed adsorbant material height, repeated studies may be necessary to determine the extent to which the increase is due to a small amount of MEA adsorbing on the edges and corner of the triangle.



Figure 25. (a) AFM before functionalization of triangular region of interest, and (b) AFM using peakforce microscopy on the same triangle after functionalization



Figure 26. (a) Height, (b) Adhesion, (c) peak force error, and (d) deformation for tungsten disulfide after functionalization triangle using peak force microscopy.

Atomic force microscopy (AFM) was also used to investigate the morphology of the new raised features on the MEA-treated multilayer tungsten disulfide after longer exposure and deposition. Two types of ridge-type features were noted and explored using Peakforce AFM which allowed much greater resolution and reduced the likelyhood of contact with adsorbant materials, unlike what would otherwise be expected of an organic layer under standard tapping mode in AFM. Normal tapping modes typically exert higher forces during measurement, leading to the risk that organic material may transfer from the substrate to the AFM tip, which could result in tip artifaction over the surface as the readsorbed organic material causes added surface area to the tip and a complicated convolution of the surface morphology to be recorded.

As shown in figure 27, the height and morphology of these ridge like features varies depending on the region they are located, and do not appear to be merely addition layers of  $WS_2$  on top of the surface. The ridges shown in the top AFM image have a very sharp contrast between the bright regions, which are between 20-40 nm above the surface, and the darker regions; additionally, these areas are spaced very close together and appear to be more striated rather than in a step-like pattern – thus suggesting that step edges alone are not sufficiently high to produce this pattern.

The second region, outlined in yellow, have a somewhat different morphology in that the bright region appears to be more globular, however, it is still solid enough to be successfully imaged by Peakforce AFM. These globular features seem to be centered around the middle line, where the adsorbant appears to have merged into a more linear feature; however, this may suggest the presensce of an adsorbant following some energetically favorable surface feature.

Another notable adsorbent feature noted on this MEA-treated WS<sub>2</sub> sample are the lighter colored triangles around 1 nm in the higher resolution SEM image of Figure 28. In the upper AFM image focused on the blue square, it is evident that the features are quite triangular in shape and may have some epitaxial growth or alignment upon tungsten disulfide below it. The particular sample under investigation is quite large, as shown in the lower resolution SEM image of Figure 27; additionally, the morphology of the edges indicates that this sample likely formed due to the merging of several "triangles" which nucleated and merged in random orientations, very close to each other, so it is reasonable that the resulting sample does not have a perfectly uniaxial surface with a well oriented



Figure 27 a. SEM image of full  $WS_2$  sample, scale bar 20 um; b. higher resolution image of  $WS_2$  with triangular features highlighted; c. region of AFM mapping with two features; d. AFM region with three features

grain. It is unlikely, however, that the prevalence of these triangles be explained by the presence of additional layers of  $WS_2$  due to their relative height, as demonstrated for the features in the great square of Figure 27. Figure 28 shows these height profiles in more detail, thus demonstrating the sharp sloping of the hill-like features, which are unlike the step-like profiles expected of additional layers  $WS_2$  that may occasionally occur on the surface of CVD grown material.



Figure 28. a. 3D mapping of three triangular "hill" features; b. placement of three height profiles; c. graph of height profiles; d. measurements of three AFM features

#### 2.3.5 EDS

Another method used for determining if the treatment of the WS<sub>2</sub> was energy dispersive X-ray spectroscopy (EDS). However, thin-layer samples of tungsten disulfide are too thin to be effectively analyzed by this method, and are prone to damage due to the higher electron beam current employed in comparison to imaging modes in the scanning electron microscopy. Instead, a thicker sample of tungsten disulfide, also functionalized at 150 sccm for 30 minutes with the same concentration of 2-mercaptoethanethiol in ethanol, was employed for this and other exploratory physical methods of probing the surface. As shown in the figure 29, there is a prominent inhomogeneity in the sulfur K-series which follows the lighter, thin regions in the electron image. A similarly shaped inhomogeneity is also present in the oxygen K-series, but also to a mild degree in the silicon K-series, thus suggesting that the thickness of the adsorbed layer may be enough to block the signal from the underlying substrate. The tungsten series presented here overlaps with both carbon and



Figure 29 a. Electron image of thicker  $WS_2$  sample, b. sulfur series with inhomogeneity, c, Si series with minor inhomogeneity, d. tungsten series with little to no visible inhomogeneity present, and e. oxygen series with inhomogeneity via an absence of signal.

sulfur and so does not show inhomogeneities, but it is presented to demonstrate that that the shape present in the sulfur series is not an artifact of  $WS_2$  system, as it would also appear as a high concentration inhomogeneity within the tungsten mapping.

#### 2.3.6 TEM Studies of Functionalized WS<sub>2</sub> Monolayers

Finally, some preliminary work has been done to explore the efficiency of this method for locating defects such as grain boundaries, line defects, and sulfur vacancies in a selective manner. WS<sub>2</sub> monolayer triangles were transferred to a Transmission Electron Microscopy (TEM) grid before treatment in order to allow for post-treatment samples to be supported on a TEM-capable substrate. Optical and photoluminescence confirmed the



TEM image of WS<sub>2</sub> grain

TEM of large triangle

Figure 30. a. TEM image of  $WS_2$  grain, b. TEM of large triangle, scale bar 2  $\mu$ m; c. Photoluminescence image of  $WS_2$  on TEM grid before treatment, scale bar 100  $\mu$ m.

presence of the  $WS_2$  on the TEM grid. Samples were then moderately treated with 2mercaptoethanethiol for 30 minutes with the argon flow rate at 100 sccm. Although the flow rate was reduce from the usual 150 sccm used for other samples, it was still high enough that some of the grid locations experienced damage during the treatment procedure. After treatment, TEM images were taken to determine if the WS<sub>2</sub> had been similarly damaged, and although during the beam-showering procedure the MEA treatment appears to have been removed, the WS<sub>2</sub> triangles themselves appear to be relatively unharmed, as shown by the TEM images in Figure 30. This implies that, due to the low electrostatic forces holding the physisorbed material to the surface, resolution of the ligand or other organic product on the surface of the WS<sub>2</sub> would not be successful as the material would not have a strong enough attraction to the surface to overcome the energy applied to the surface during electron beam showering when performing the for measurement.

## 2.4 Closing Remarks

In summary, it has been determined that the reaction as described in scheme 2, in which physisorption of applied organic material ensues after a surface-catalyzed reduction of the preliminary thiolated ligand 2-mercaptoethaneamine was exposed the surface of monolayer WS<sub>2</sub>. A thorough comparison of samples of tungsten disulfide, which have been grown by CVD, before and after exposure to the 2-MEA, indicates that the thiol group of the ligand react on the WS<sub>2</sub> surface to produce a disulfide reaction product which remains physisorbed to the surface. The reduction of two thiol groups of separate ligand molecules

produces not only the disulfide bearing product, but also permits the loss of electrons, some of which may transfer to the surface of the semi-conducting WS<sub>2</sub>. This increase in charge carriers can be observed through the close analysis of the changes in the LA mode of the Raman spectra, such as a loss of intensity and blue shift in the LA Raman mode. These changes indicate that there is an increase of charge carriers, thus presenting a loss in the band intensity, along with a blue shift due to corresponding to the transfer of energy to the surface. The total loss of the 2LA band also reflects this shift. The broadening of the  $E_{2g}$ can also be understood as the local anisotropy of the functionalization (as shown in the Raman mappings of figure 18), would lead to a broadening in the overall range of energy for in-plane electronic transitions. Furthermore, through comparisons of samples examined by XPS, there was an increase in the content of the nitrogen (and therefore sulfur) only on the treated surfaces. These results from XPS re also in agreement with those obtained from ToF-SIMS, where the low presence of the single ligand and the reduction product are countered by the relatively high intensity of the reduction product's main fragment. This has been determined by comparing mass spectra with and without treatment on regions containing WS<sub>2</sub>, and theoretical calculations for the mass isotope distributions, that the predominant fragment of the reduction must be the result of cleavage between a sulfur of disulfide bond, and a neighboring carbon atom bonded to the sulfur. the This is expected due to shift in electron density towards the disulfide bond and away from the bond to the nearest sp<sup>3</sup> hybridized carbon. AFM was used to rule out the presence of excess material as well as to characterize the topography of high-concentration agglomerations of the ligand and ligand reduction product. Aberration corrected HRTEM was attempted to characterize the sample, however due to the low electrostatic forces

holding the physisorbed material to the surface, resolution of the ligand or other organic product on the surface of the  $WS_2$  was not successful. Thus, we have provided evidence that physisorption of the post-reduction material must have occurred, and an in-lattice substitution or chemisorption is not the expected product of this treatment.

### 2.5 Bibliography

- Knirsch, K. C.; Berner, N. C.; Nerl, H. C.; Cucinotta, C. S.; Gholamvand, Z.; McEvoy, N.; Wang, Z.; Abramovic, I.; Vecera, P.; Halik, M.; *et al.* Basal-Plane Functionalization of Chemically Exfoliated Molybdenum Disulfide by Diazonium Salts. *ACS Nano* 2015, *9*, 6018–6030
- Cho, K.; Min, M.; Kim, T.-Y.; Jeong, H.; Pak, J.; Kim, J.; Jang, J.; Yun, S. J.; Lee, Y. H.; Hong, W.; *et al.* Electrical and Optical Characterization of MoS<sub>2</sub> with Sulfur Vacancy Passivation by Treatment with Alkanethiol Molecules. *ACS Nano* 2015, 8044–8053.
- Chou, S. S.; De, M.; Kim, J.; Byun, S.; Dykstra, C.; Yu, J.; Huang, J.; Dravid, V. P. Ligand Conjugation of Chemically Exfoliated MoS<sub>2</sub>. *J. Am. Chem. Soc.* 2013, *135*, 4584–4587.
- Kim, J. S.; Yoo, H. W.; Choi, H. O.; Jung, H. T. Tunable Volatile Organic Compounds Sensor by Using Thiolated Ligand Conjugation on MoS<sub>2</sub>. *Nano Lett.* 2014, *14*, 5941–5947.
- Ding, Q., Czech, K. J., Zhao, Y., Zhai, J., Hamers, R. J., Wright, J. C., & Jin, S. (2017). Basal-Plane Ligand Functionalization on Semiconducting 2H-MoS <sub>2</sub> Monolayers. ACS Applied Materials & Interfaces, acsami.7b01262.
- Sim, D. M., Kim, M., Yim, S., Choi, M. J., Choi, J., Yoo, S., & Jung, Y. S. (2015). Controlled Doping of Vacancy-Containing Few-Layer MoS<sub>2</sub> via Highly Stable Thiol-Based Molecular Chemisorption. *ACS Nano*, 9(12), 12115–12123.
- Berkdemir, A.; Gutiérrez, H. R.; Botello-Méndez, A. R.; Perea-López, N.; Elías, A. L.; Chia, C.-I.; Wang, B.; Crespi, V. H.; López-Urías, F.; Charlier, J.-C.; *et al.*, (2013), Identification of Individual and Few Layers of WS<sub>2</sub> Using Raman Spectroscopy, *Sci. Rep.*, *3*, 1755.

## Chapter 3

## **Conclusion and Future Outlook**

#### **3.1 Mechanism and Implications**

Through the work described, it has been determined that the reaction dominated by physisorption after a surface-catalyzed reduction of the thiolated ligand occurs after application of the ligand 2-mercaptoethaneamine onto the surface of thinlayered tungsten disulfide. Thus, there is strong evidence to suggest that the mechanism described as scheme 2 (fig 7) occurs within the system of 2-MEA functionalizing WS<sub>2</sub>. By enacting a detailed assessment of thin-layered tungsten disulfide, strongly indicate that the thiol group of the ligand react on the surface to produce a disulfide reaction product which remains physisorbed to the surface after this reaction<sup>1</sup>. These TMD samples have been grown by chemical vapor deposition and characterized before and after exposure to the 2-MEA. The reduction of two thiol functional groups of separate ligand molecules produces both the disulfide bearing product, but also permits the opportunity for a transfer of some electrons to surface of the semi-conducting tungsten disulfide. This increase in charge carriers has been primarily detected through the changes in the LA mode of the Raman spectra, such as a loss of intensity and blue shift in the defect-describing band. These differences indicate that there is an increase of charge carriers, thus presenting a loss in the band intensity, along with a blue shift due to corresponding to the transfer of energy to the surface. The loss in intensity for the 2LA

band also reflects this shift, as there is a significant decline of intensity relative to the previous location of the LA band. The broadening of the  $E_{2g}$  band also suggests that the local anisotropy of the regions of functionalization-based variances (as shown in the Raman mappings of figure 18), would lead to a broadening in the overall range of energy for in-plane electronic transitions. Furthermore, through the comparisons of samples characterized by XPS, an increase in the content of the elements nitrogen and sulfur is noted, as would be expected for the added presence of the thiol and amine bearing compound which appears only on the surfaces which have been treated. These results from XPS are also supported by the complementing ToF-SIMS study, where the unexpectedly low presence of the single ligand and the reduction product are offset by the relatively high intensity of the reduction product's main fragment. This has been determined through use of comparison between mass spectra with and without treatment on regions bearing tungsten disulfide, and theoretical calculations for the mass isotope distributions, that the predominant fragment of the reduction must be the result of cleavage between a sulfur of the disulfide bond, and a neighboring carbon atom bonded to the sulfur, as would be expected due to shift in electron density toward the disulfide bond and away from the bond to the nearest sp<sup>3</sup> carbon. Furthermore, AFM was used to rule out the presence of excess material as well as characterize the topography of highconcentration agglomerations of the ligand and ligand reduction product. While TEM was attempted to characterize the sample, the relatively low electrostatic force between physisorbed material and the TMD surface led to difficulty in resolving the ligand or other organic product on the surface of the tungsten disulfide. Thus, it is clear that physisorption of the post-reduction material must have occurred, and an in-lattice

substitution or chemisorption is not the expected product of this treatment. It can be concluded that the reduction and physisorption of scheme 1 dominates the behavior of this system.

## **3.2 Future Work**

This work focused heavily on 2H- WS and relied on several novel works on  $MoS_2$ ; however, the functionalization of a large majority of TMDs have not yet been addressed. Several avenues of study will need to be carried out in order to fully determine if the treatment described is an effective method of selective TMD functionalization. A systematic study of the effects of the concentration of the MEA in ethanol, or other ligand/solvent combinations as described below, will need to be performed in order to determine if varying the concentration can improve the selective adsorption for different



Figure 31. Schematic for new two-input treatment system. One input will control the flow of argon through the bubbler of the thiolated organic material while a second controls an independent input for argon to permit greater control of the concentration of the ligand during treatment without compromising the flow rate for exposure.

types of TMDs. In combination with the presented work on varying the flow rate, this should permit much greater control over the treatment of  $WS_2$  with thiolated ligands.

Additionally, careful HRTEM studies would provide more insight into the efficiency of adsorbants to determine surface features such as defects that could speed up the reaction, thus permitting a non-destructive alternative for locating defective sites<sup>2</sup>. It is expected that using SEM and AFM before and after TEM, areas where the depositions occurred could be located quickly and easily identified as has already been demonstrated in Fig. 30. Then after TEM, SEM and AFM, and Raman studies it will be possible to determine the amount of adsorbant remaining. Further studies with XPS and ToF-SIMS are also needed for determining if these monolayer TMDs behave similarly to the previous experiments on MoS<sub>2</sub> and WS<sub>2</sub>.

By removing 2-MEA and replacing it with similar thiolated ligands to witness if the presence of other functional groups improves the electronic and optical properties of the WS<sub>2</sub>. To this effect, a two-input system such as the one laid out in figure 31 would be employed to allow two lines of argon to be run either individually (one with, and one without, flow through the bubbler), or to be combined for greater control of the net amount of ligand capable of entering the system. Two specific ligands of interest are 1H, 1H, 2H, 2H-perfluorodecanethiol (FDT) and 2,2,2-trifluoroethanethiol (TFET), both of which are fluorinated ligands that use tetrahydrofuran as a carrier solvent, and Argon as the carrier gas. Similar characterization methods as those used for the MEA could be carried out for the FDT and TFET in order to compare the electronic effects these ligands would have. If similar reduction processes occurred as did with 2-MEA on WS<sub>2</sub> on the surface of a selected TMD with additional electron rich moieties, it might increase the effect that such electron donation at the surface would have on electronic structure of the material; see the previous shifts shown in the Raman study above (see chapter 2, figures 16-19). These shifts may be able to be quantified by the strength of the competing moieties. If there should be additional side reactions between the thiol, the surface, or the exchange moiety, such a difference would be able to be investigated by Raman Spectroscopy, XPS, and ToF-SIMS.

Finally, the ligand with the most optoelectronic interest or which showed the best signs of chemisorption to functionalize both  $MoS_2$  and a lateral heterostructure of  $MoS_2$  and  $WS_2$  (figure 32). The  $MoS_2$  would be a point of comparison for the lateral heterostructure and for the  $WS_2$ , as many reports in the literature for chemisorption and adsorption of thiolated ligands currently focus exclusively on  $MoS_2$  acquired from non-CVD methods such as mechanical exfoliation or lithium intercalation. It would be expected that any adsorption would occur on the edge or near the interface of the  $MoS_2$  and  $WS_2$ , and  $WS_2$ , and  $WS_2$  a



Figure 32 Schematic of selectively thiolated lateral heterostructure. The lateral heterostructure follows a core-shell structure such that the inner core of  $MoS_2$  is surrounded by an outer layer of  $WS_2$ . The boundary of these two regions is highlighted in red to illustrate the enhanced PL at this interface. Thiolated ligands are placed at various high defect-density regions such as the interface and edges of the lateral heterostructure, illustrating regions where selective adsorption of the ligands may occur.

which is reported to be atomically sharp<sup>3</sup>. These interfaces and edges would be anticipated to have a higher occurrence of defects due to the change in lattice parameter between the regions, so it would be anticipated that this region is favorable for a defect-directed adsorption of applied thiolated ligands. Furthermore, adsorption near the interface, which has been reported to have improved PL, would better display any charge carrier injection from an applied ligand.

## 3.3 Bibliography

- Chen, X., McDonald, A. R. (2016). Functionalization of Two-Dimensional Transition-Metal Dichalcogenides. *Advanced Materials*, 28(27), 5738–5746.
- Rong, Y.; He, K.; Pacios, M.; Robertson, A. W.; Bhaskaran, H.; Warner, J. H. Controlled Preferential Oxidation of Grain Boundaries in Monolayer Tungsten Disulfide for Direct Optical Imaging. *ACS Nano* 2015, *9*, 3695–3703.
- Gong, Y.; Lin, J.; Wang, X.; Shi, G.; Lei, S.; Lin, Z.; Zou, X.; Ye, G.; Vajtai, R.; Yakobson, B. I.; *et al.* Vertical and in-Plane Heterostructures from WS<sub>2</sub>/MoS<sub>2</sub> Monolayers. *Nat. Mater.* 2014, 1–33