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Synthesis of Two-Dimensional Molybdenum Disulfide Nanostructures Using Molybdenum Trioxide Thin Film Via Chemical Vapor Deposition

Vanessa Charles
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SYNTHESIS OF TWO-DIMENSIONAL MOLYBDENUM DISULFIDE NANOSTRUCTURES USING MOLYBDENUM TRIOXIDE THIN FILM VIA CHEMICAL VAPOR DEPOSITION

by

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B.S. University of Central Florida, 2017

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ABSTRACT

Two dimensional (2D) materials-based nanostructures have attracted much attention due to their unique properties which exhibit promising prospects for application in catalysis and energy storage devices. Control growth method is important in synthesizing these nanostructures. Chemical vapor deposition (CVD) is a powerful method that provides scalability and controllable way to grow high quality 2D materials-based nanostructures. Here, we report a novel CVD growth method of 2D molybdenum disulfide (MoS$_2$) based different structures in which thin film of molybdenum trioxide (MoO$_3$) was used as the source of molybdenum (Mo), while sulfur (S) powder was used for the chalcogen precursor. Precise control of Mo precursor which is hard to achieve with MoO$_3$ powder promotes high quality growth of MoS$_2$ based nanostructures. In particular, we observed different MoS$_2$-based nanostructures under different growth conditions. The structures were characterized by a variety of techniques to identify their chemical composition and structural nature. Scanning electron microscopy showed the morphology of the vertical plates, nanocrystals, and triangles structures. Raman spectroscopy indicated that the MoS$_2$ based vertical plates are composed of MoO$_2$ and MoS$_2$. Transmission electron microscopy confirmed the multilayer shell of MoS$_2$ with MoO$_2$ core in the nanocrystal structures. We have successfully grown these nanostructures using precise control of the precursor concentration in confined vapor phase. These nanostructures could be relevant in the application of electrocatalytic materials with insufficient long-range conductivity, such as water oxidation catalysts consisting of poorly conducting metal oxides. Confined vapor phase paves the way to control surface structures of MoS$_2$ at the nanoscale to ultimately develop effective catalyst-based materials with high densities of active edge sites at the surface.
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CHAPTER 1: INTRODUCTION

1.1 Overview

Two-dimensional (2D) monolayer materials transition metal dichalcogenides (TMDCs) have acquired a great deal of attention in the fields ranging from fundamental studies of charge transport to next generation optoelectronic devices and catalysis [1]. In particular, 2D molybdenum disulfide (MoS$_2$) has been vastly studied and extensive reports have focused on the growth of mono- or few layers of MoS$_2$ films [2]. The layered structure of the MoS$_2$ crystal can give rise to different structures which range from nanocrystals to nanotubes and vertical plates [3, 4]. Additionally, significant efforts have been made in modifying the structures of MoS$_2$ for use as an electrocatalyst, solar cell materials, and in Li-ion batteries [4]. Recently, capacitors research has focused on MoS$_2$ based nanostructures due to their higher intrinsic fast ionic conductivity [5]. Furthermore, the development of synthesis method which enable the precise control of MoS$_2$ structural properties such as size, increasing in high surface area, and increasing in active sites are key areas to address during the growth process.

1.2 Transition Metal Dichalcogenides

TMDCs are a class of layered compound with the formula of MX$_2$ where M is the metal such as Mo, Sn, W etc. and X is the chalcogen such as S, Te, Se etc. The library of TMDCs family is highlighted in Figure 1 focusing on the mostly used transition metal and chalcogen [1]. These layered materials may exhibit conducting, metallic, or semiconducting properties depending on the selection of the metal [6]. Depending on the thickness of the layered materials, their semiconducting properties may vary. Their unique optical and electronic properties have potential in the applications of optoelectronics, catalysts, sensors and transistors [7, 8]. In TMDCs, the
transition metal atoms are covalently bonded to the chalcogen atoms within the same layer [1, 9]. TMDC materials can be functionalized to achieve different purposes such as drug delivery agents, therapeutics, bio-imaging and as well as biosensors [1, 10]. The functionalization of TMDCs is possible because of their large surface-to-volume ratio which provides access for their chemical modifications [1]. TMDCs can take on a variety of structural motifs and are considered to be potential alternatives catalyst based materials [11, 12].
Figure 1: Periodic table with highlighted transition metal and chalcogen elements. Copyright 2016, with permission from Elsevier [1].

MoS$_2$ is the most abundant and extensively studies of the TMDCs family. The physical crystal structure of TMDC material particularly MoS$_2$ is depicted in Figure 2. The layer of the transition metal atom is sandwiched between two layers of chalcogen atoms which are coupled by van der Waals forces [1, 9]. Additionally, there is no dangling bond on the surface of the layer of TMDC materials which allows for their stability against reactions with environment species even when it is thinned down [1, 13]. The electronic band structure of TMDCs can change from indirect as in the bulk to direct band gap when the material is thinned to a single layer [1, 9]. The transition from indirect to direct band gap arises from quantum confinement effects and observes as enhanced photoluminescence (PL) yield in single layer TMDCs [1, 13]. The conductivity of MoS$_2$ in a high surface area structures presents a challenge as the conductivity of MoS$_2$ along certain
crystallography directions is poor [7]. The sheet-like morphology of MoS$_2$ provides large surface area for double layer charge storage which make it great candidates for electron materials in supercapacitors [5].

Figure 2: Structure of MoS$_2$ crystal. Copyright 2016, with permission from Elsevier [1].

Different structural motifs can be created from the layered Mo-S-Mo crystal structure such as nanoclusters, nanotubes, nanoflowers, nanoflakes, nanosheets [11, 14-17]. The bulk surface of MoS$_2$ is known to be catalytically inert and consists of basal plane sites [11]. Additionally, the basal plane could be orientated to the substrate either parallel or perpendicular [11]. In contrast, the edges of the layered MoS$_2$ have high catalytic activity particularly for hydrogen evolution reaction (HER) [8-14]. Therefore, recent studies have focus on creating MoS$_2$ based nanostructures with accessible edge sites [6-15]. Hybrid nanostructures compose of two different materials such
as MoO\textsubscript{2}/MoS\textsubscript{2} structured nanomaterials, can be used to construct efficient and stable HER catalysts from easily available compounds [5, 14, 17, 18].

Furthermore, hybrid MoS\textsubscript{2} nanostructure has high density structural defects and disorders on the outer layer (shell) which is usually composed of MoS\textsubscript{2} that generates fully exposed active sites [19, 20]. Additionally, the structural defects of hybrid MoS\textsubscript{2} nanostructures are due to mismatch of the crystals in the inner layer (core) which is usually composed of MoO\textsubscript{2} material [20, 21]. Recent research found that MoO\textsubscript{2} core enhances the stability of the hybrid MoS\textsubscript{2} nanostructures [3, 14]. Also MoO\textsubscript{2} is metallic and facilitates charge transport for proton reduction in HER by reducing the number of interfaces [22-25]. Additionally, MoO\textsubscript{2} may increase the electronic conductivity of MoS\textsubscript{2} nanostructures which also provides a larger surface area to volume ratio [15, 17].

1.3 Objective of the thesis

The aim of this thesis is to elucidate different MoS\textsubscript{2} based nanostructures using precise control of Mo vapor pressure by means of MoO\textsubscript{3} thin film for Mo precursor. Additionally, chemical vapor deposition (CVD) method was used to synthesize these nanostructures following the three steps chemical reactions pathways. This approach enabled the growth of nanoplates, nanocrystals, and monolayer MoS\textsubscript{2} on silicon substrate. Additionally, we elucidated the growth mechanism of MoS\textsubscript{2} nanostructures based on the design of the CVD growth process.
1.4 Overview of the thesis

This work reports on the synthesis of 2D MoS$_2$ nanostructures using a novel CVD method that provide uniform control of the vapor pressure of the precursors. An overview of TMDCs properties, synthesis methods, and their potential application are described. Chapter two provides background information on different types of molybdenum disulfide (MoS$_2$) preparation methods. Chapter three details the chemical vapor deposition method and the experimental setup. Chapter four provides the experimental results, which include Raman spectroscopy and scanning electron microscopy characterization of the 2D MoS$_2$ nanostructures. Chapter five explains the future perspective of this work which may have the potential contribution as electrocatalysts for hydrogen evolution reaction.
CHAPTER 2: MoS₂ PREPARATION

2.1 Overview

Electrocatalyst development has become significant in the production of energy devices due to electrochemical conversion reactions [23]. Electrocatalytic water splitting using a carbon free system presents a more promising solution for producing hydrogen [22, 23]. There is a significant challenge in the development of a single material that can provide high photon to current conversion, catalytic activity, and stability [1]. The stability of the hydrogen evolution catalyst in chosen electrolyte is a key component which is necessary in the driving of current densities that match the solar photon flux at low overpotentials [22]. Conventional hydrogen evolution catalysts currently consist of platinum or platinum-based materials which can drive hydrogen evolution reaction (HER) due to excellent kinetics. Various examples of metal catalyst include metal sulfides, metal phosphides, metal carbides, and heteroatom-doped carbons [22]. The alternative materials such as nickel mostly work with alkaline electrolyte. However, the use of platinum may be limited due to high cost therefore the need for easily available metal alternatives remains attractive. Molybdenum disulfide (MoS₂) nanostructures have been intensively studied as a potential metal-based electrocatalysts. In addition, the properties of MoS₂ based nanostructures depend on their structures such as sizes, morphologies, orientations, defects, and number of layers [6, 9, 17, 26]. Therefore, recent works have focused on creating MoS₂ based nanostructures with high number of active sites and enhanced electrocatalytic activity [11, 23].
2.2 Morphology

Molybdenum disulfide (MoS\textsubscript{2}) is a layered 2D TMDC material that has poor activity for HER in the bulk form [1]. However, recent studies have demonstrated that nanoparticles of MoS\textsubscript{2} exhibit excellent activity for the HER which were associated with their exposed edge sites [1]. It was determined that the exposed edge sites are the active site responsible for the catalytic activity. As a result of these studies, MoS\textsubscript{2} based catalyst materials have attracted a great deal of interest. In the past years, significant progress has been made in synthesizing MoS\textsubscript{2} catalysts materials with efficient HER performances [22, 23]. There is focused on maximizing active site densities of MoS\textsubscript{2} catalyst using structural engineering approaches such as space-confined growth, vertical alignment, and self-assembly [22]. Depending on the size of the MoS\textsubscript{2} nanosheets, the coverage of sulfur atoms on the edges of MoS\textsubscript{2} varies. Additionally, it has been demonstrated that sulfur coverage on the edges can affect the adsorption of hydrogen (H) atoms significantly which is directly correlated to HER kinetics [2]. The conductivity of MoS\textsubscript{2} in a high surface area structures presents a challenge as the conductivity of MoS\textsubscript{2} along certain crystallography directions is poor [1]. To improve this limitation, hybrid MoS\textsubscript{2} structures with metal oxide core and MoS\textsubscript{2} shell is of need. In addition, there are two commonly orientations of the basal plane of MoS\textsubscript{2} which are parallel or perpendicular [14]. Previous studies of MoO\textsubscript{3}-MoS\textsubscript{2} nanowires have shown for the most part that if the basal plane is parallel to the nanowire axis, there is limitation to the number of edge sites exposures [1]. Therefore, nanoparticles of MoS\textsubscript{2} with basal plane perpendicular to the axis which have more exposure of the edge sites is of interest [5]. Furthermore, surface modification of MoS\textsubscript{2} can improve its dispersion and processability properties which make the use of MoS\textsubscript{2} based nanostructures unique and are also good functionality for high performance capacitors [5].
2.3 Synthesis Methods

Recently, there has been significant progress being made in synthesizing highly active and stable electrocatalyst whose structures mimic the active sites of natural catalysts such as nitrogenase enzymes [1, 27]. To date, MoS$_2$ has been synthesized on different substrates by various methods such as mechanical exfoliation, liquid exfoliation, hydrothermal treatment, and chemical vapor deposition (CVD). Hydrothermal synthesis produces crystals which depends on the solubility difference of an aqueous solvents with the starting materials under high pressure [7]. Wang et al. used this technique to grow nanostructures of MoS$_2$ hybrids [12]. Additionally, Huang and co-workers had used hydrothermal synthesis method to produce MoS$_2$/graphene nanocomposites with enhanced capacitive performance [5]. Moreover, Kumar et al. performed plasma-assisted sulfurization of MoO$_3$ to obtain MoO$_2$/MoS$_2$ nanoflakes [21]. However, the synthesis of the MoS$_2$ nanostructures using those methods resulted in multistep procedures [7, 21].

Mechanical exfoliation method has been widely used to produce MoS$_2$ flakes. TMDCs atomic layers can be exfoliated mechanically or with the use of solvents. The mechanical exfoliation technique, using scotch tape by applying mechanical forces to peel off few or single layers of flakes from bulk materials, produces intrinsic flakes that have good quality [1-5]. However, some of the flakes can be broken up during exfoliation and may be generally small. Additionally, this approach is limited in terms of production of MoS$_2$ based nanostructures with accessible edge site.

Liquid exfoliation is another method used to peel off layers of MoS$_2$ by sonication in solvents to disperse the layers [9]. During a direct sonication, the breaking of the TMDCs layers depend on the solvent of choice to overcome the cohesive energy between individual layers [4]. Furthermore, the properties of the selected solvents including solubility, surface tension, and
boiling point affect the process [28]. Bayat et. al. used ultrasonic liquid exfoliation process to synthesize MoS$_2$ nanoflakes [28]. However, their process required high voltage to obtain vertical deposition of MoS$_2$ nanoflakes on the substrate [28]. Another type of liquid exfoliation is electrochemical exfoliation in which small ions like Li$^+$ are driven into the interlayer of the TMDCs to reduce the bonding strength and exfoliate the layers. Proteins can be used to exfoliate due to their polarity effect when bonded on TMDCs in water [3]. Residual contaminations may remain during liquid exfoliation techniques which may cause structural defects such as vacancies in the exfoliated TMDCs [9, 29].

Chemical vapor chemical (CVD) is the most popular chemical method which involves the vapor phase reaction from a metal oxide (MoO$_3$, WO$_3$) and chalcogen (S, Se, Te) [13, 26, 30-32]. CVD method proved to be cost effective and efficient to synthesize TMDCs of interest [26, 33]. This method has proven to be very versatile in producing large area synthesis of TMDCs as well as their alloyed and heterostructures [34]. As demonstrated by Zhong and co-workers, they synthesized MoS$_2$ nanoflowers on carbon papers using CVD method [35]. However, gold nanoparticles were needed to produce denser and larger area MoS$_2$ nanoflowers. Moreover, Nikam et. al. synthesized MoS$_2$ nanosheet on three dimensional conductive MoO$_2$ using a two-step CVD reaction on carbon cloth [3]. In addition, Wang and co-workers were able to synthesize MoSe$_2$ nanomaterials on Si/SiO$_2$ substrate using hot filament CVD method for better control of the temperature of the precursors [36]. However, the variation in molybdenum (Mo) concentration changes the morphologies of the nanomaterials observed. Parks et. al grew vertical MoO$_2$/MoS$_2$ crystals on amorphous SiO$_2$ substrate at a high heating rate using a confined configuration [4]. DeGregorio and co-workers grew MoO$_2$/MoS$_2$ core-shell nanoplates via epitaxial interaction with a given substrate [37]. Additionally, they explained that the growth of the vertical structures is due
to interactions between substrates and MoO$_2$ core. Furthermore, the orientation of the nanoplates were formed randomly at the borders of the substrates. However, these syntheses require specific substrates and lack of control of Mo vapor pressure are drawbacks for achieving highly efficient MoS$_2$ nanostructures.

![Ternary phase diagram for Mo – S– O showing the possible reactions to produce MoS$_2$.](image)

Figure 3: Ternary phase diagram for Mo – S– O showing the possible reactions to produce MoS$_2$.

In the CVD process, the reaction of MoO$_3$ with S occurs in the vapor phase which then produce TMDCs following the three-stages chemical reactions [38]. In the first stage, MoO$_3$ is partially reduced and formed volatile oxide/oxysulfide particles followed by the second stage in which MoO$_3$ is further reduced and sulfurized to MoS$_2$ at optimal S condition and in the final stage, MoO$_3$ is completely reduced to nonvolatile particles. The reaction path is shown in Figure 4 and the potential pathways for the reaction is shown in Figure 3. If during the second stage, the S condition is not optimal, S deficient, the synthesized product will be MoS$_2$ hybrid particles. Therefore, the concentration of S vapor will determine the outcome of the growth process [38]. Additionally, maintaining uniform vapor pressure of the precursors is highly desirable for controlling Mo/S ratio [29].
Figure 4: Potential pathways for reaction of MoO$_3$ and chalcogen.
CHAPTER 3: CHEMICAL VAPOR DEPOSITION

3.1 Overview

Solution phase synthesis has been investigated for highly actives MoS2. However, vapor phase route remains the most attractive method to explore due to high interface quality with desired substrates and large-scale productivity [1]. Hydrothermal treatment method results in irregular particles. Unlike the other method for MoS2 nanostructures preparation, CVD provides less time during synthesis and less sample treatment. CVD method is the most popular method that proves to be cost effective and efficient in synthesizing MoS2 2D nanostructures. CVD method is a bottom-up approach in which source materials are heated and evaporated in a reaction chamber and onto a target substrate [39]. The evaporated materials are carried out by inert carrier gases where the reaction happens between chemical precursors [9].

In the most conventional CVD setup, heat is applied in the furnace and solid powdered based TMDCs and chalcogens are used. CVD method consists of four steps to grow TMDCs which are 1) the chemical sources evaporate into the carrier gas, 2) the chemicals react with sulfur to produce MoO$_{2-x}$S$_x$, 3) MoO$_{2-x}$S$_x$ diffuses into the carrier gas and deposits onto the target substrate, 4) MoO$_{2-x}$S$_x$ reacts with the target substrate to initiate the nucleation step then growth of 2D TMDCs flakes [9]. CVD synthesis methods include thermal decomposition of thiosalts and thermal vapor sulfurization of Mo/MoO$_2$ thin films [40]. However, this method lacks control of uniform vapor pressure of the precursors, specifically Mo vapor pressure. Therefore, the control of precursor concentration, rate of carrier gas, growth temperature, and configuration of substrate are challenging and are needed to optimize the growth of TMDCs. Additionally, the importance of
controlling sulfur vapor has been investigated vastly in the literature, but the control of Mo vapor is very scarce [4].

3.2 Parameters

The key parameters that govern CVD method include concentration of the precursors, the rate of the carrier gas, growth temperature, and the configuration of substrate which are depicted in Figure 5 [1, 9]. The properties of TMDCs depend on their morphology, size, phase and any interfaces present [9]. Therefore, it is important to understand the general mechanism of CVD growth specifically how the key parameters affect the growth of the materials. Figure 5 shows how various parameters including precursor, temperature, and pressure affect the CVD growth of 2D materials. Precursors serve as reactants in the process and are carried to the substrate using carrier gas such as N₂ and Ar gas [9, 41].

The precursors require accurate temperature control since the vapor pressure is extremely sensitive to temperature variation during the growth [1]. Additionally, the higher the temperature, the chemical reaction rate also increased due to higher gas concentration as well. The temperature of the substrate can also induce variation in the adsorption of the precursors since the lattice structure of the substrate can affect the growth of the materials [9]. Furthermore, seed promoters such as PTAS and sodium chloride can be used to promote adsorption and nucleation of the precursors on the substrate [26, 30]. Therefore, optimization and carefully control those parameters are important for CVD growth of TMDCs of specific target morphology, size, and large area growth.
Figure 5: Schematic of various parameters in the CVD growth method. Reprinted from ref [9].

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3.3 Experimental setup

The synthesis of the nanostructures was carried out in the CVD system depicted in Figure 5a. Si substrates with 250 nm thick oxide layer as growth substrate as well as the substrates to deposit the MoO$_3$ thin films which were used as a precursor for molybdenum source. Both source and substrate were cleaned using sonication in acetone for 10 min, followed by sonication in isopropyl alcohol for 5 min, deionized water rinse, and 10 min mild oxygen plasma treatment. MoO$_3$ thin films with 20 nm thickness were deposited using thermal evaporation of MoO$_3$ powder (99.5%, Sigma-Aldrich) in a vacuum chamber at low evaporation rates of 0.25 A/s. The substrate was coated with PTAS, seed promoter, by placing one drop of PTAS on the cleaned substrate and dried using flow of nitrogen gas.

The thin film deposited substrates were cut to 5 mm x 5 mm size and placed in a quartz boat; coated substrates were placed on the same boat facing down and placed at the center of the furnace. Although the front end of the boat was left open for sulfur vapors to enter the reaction zone easily, the rear end was covered by the substrate to trap the vapor phase precursors near the substrate which is the photograph image in Figure 5c. Quartz crucible containing 400 mg of sulfur powder (99.5%, Sigma-Aldrich) was loaded into the opening of a single-zone tube furnace (Lindberg Blue M) upstream at low-temperature zone.

The temperature profile for S is shown in Figure 5b. The MoO$_3$ and S precursor distance (r) is adjusted accordingly such that S starts melting below 100°C from the growth temperature. The carrier gas was Argon gas (99.995% purity). The temperature of the furnace was raised to the growth temperature of 750°C at the rate of 20°C/min and held for 5 min (dwell time). After the dwell time, the furnace was cooled down naturally until the temperature dropped to 500°C at which, the furnace hood was opened for rapid cooling. The Ar flow rate was kept constant during
the experiments. For the parameters used in this process, it was determined that 10 sccm gas flow with 5 min dwell time was optimal for our growth.
Figure 6: Experimental setup. a) schematic representation of the atmospheric pressure CVD setup and the relative S, MoO$_3$ and substrate positioning. b) The temperature profile at the center of the furnace. c) Photograph of the boat containing MoO$_3$ thin film covered with a substrate in a confined vapor-phase reaction configuration.
3.4 Characterization

There are many characterizations technique practice for 2D TMDCs materials such as scanning electron microscopy (SEM), Raman spectroscopy, and transmission electron microscopy (TEM). Each of those characterization techniques provide different understanding of the materials composition and structures. The basic concept of SEM is to scan a sample using focus electron beam under an accelerating voltage, aperture, working distance, and signal detector to acquire images with topography information of the sample. The MoS$_2$ based nanostructures were scanned using Zeiss Gemini 500 SEM instrument with an accelerating voltage of 5.0 kV and low current because at a higher voltage there was electrons discharge on the sample which affect the resolution of the image. The selected aperture, working distance, and signal detector were 20 nm, 5 mm, and InLens detector, respectively. Figure 7 showed SEM images of samples of MoO$_3$ annealing at different temperature.

Raman spectroscopy characterization is another technique used to get a more definite results of the chemical compositions of 2D TMDCs materials by identifying their vibrational energy. The Raman spectroscopy analysis were performed at room temperature using Raman Renishaw Invia microscope. The excitation wavelength was 514.5 nm from an Ar laser. The scattered light was dispersed off a 1200 groove/mm grating inside 800 mm spectrograph and imaged onto a CCD camera. The focused laser spot size on the samples was about 600 nm.

TEM was used to identify the number of layers and layers spacing of MoS$_2$ in the nanostructures. The cross-sectional samples used in the scanning/transmission electron microscope (S/TEM) analyses were prepared by nonstandard FIB lift out procedures. Here, an electron activated glue (SEMglue$^{\text{TM}}$) was first applied to the film to ensure complete entombment of any crystals present on the surface. Then, a thin blade of material was lifted from the surface,
exposing the film and attached nanoparticles grown there in cross section. This blade was placed on a copper TEM grid for further thinning in the FIB by standard processing steps. Energy dispersive X-ray spectroscopy (EDS) mapping and analyses were carried out using a Thermo Scientific™ Talos F200X S/TEM equipped with the ChemiSTEM™ system. Bruker-Esprit software was used to collect the maps displayed in the present work.
CHAPTER 4: EXPERIMENTAL RESULTS

The formation of the nanostructures is determined by the rate of the vapor pressure of sulfur in the CVD. During the growth process, the reaction between Mo and S occurs in the vapor phase. The distance of S to MoO₃ source was carefully adjusted to introduce sulfur when the center of the furnace was at 650°C to ensure that MoO₃ thin film sublimed before S enters the reaction zone. In addition, systematic control experiments were conducted with no S where dwell time and flow rate parameters were similar of the optimal growth process. Figure 7 shows SEM images of MoO₃ annealing samples at different temperature. The SEM analysis indicated at which temperature the source substrate completely sublimed. We found that at temperature of 550°C, MoO₃ thin film evaporated completely. As a result, using this method ensures uniform vapor pressure throughout the growth process. The effect of S precursor amount was tested by varying S concentration from, 50, 100, 200, 300, to 500 mg using 20 nm MoO₃ thin film. However, the nanostructures were still observed which suggesting that uniform Mo vapor pressure was maintained at various S concentration.
Figure 7: Optical and SEM images of MoO$_3$ thin film annealing at 400$^\circ$C, 450$^\circ$C, 500$^\circ$C, and 550$^\circ$C temperature.
4.1 Nanoplates

In previous study by DeGregorio et al., vertical crystal growth was obtained by epitaxial interaction with underlying substrate. However, in this present method, vertical crystals growth could be achieved directly on the amorphous SiO$_2$ substrate. The morphology of the structures is studied using scanning electron microscopy (SEM). The structures of the MoS$_2$ nanoplate show vertical orientation as observed by SEM in Figure 8. In addition to the nanoplates grown on the growth substrate, we have observed vertical nanoplates growth on source substrate (Figure 8d-f) as well, although the structures are less dense compare to the growth substrate. We hypothesize that this observation is due to the unique geometry of our growth substrate where Mo and S vapors are trapped between the confined space of the growth substrate to the source substrate.
Figure 8: Growth Results. SEM images showing the 2D MoS$_2$ nanostructure grown on (a,b,c) substrate and (d,e,f) thin film source.
Raman spectrum is used as an analytical tool to identify the chemical composition of the nanoplates. The Raman spectrum shown in Figure 9 reveals that most of the vertical nanoplates consist of MoO$_2$. Additionally, the peaks shown in the spectrum at 200.1 cm$^{-1}$, 225 cm$^{-1}$, 362.3 cm$^{-1}$, 455.3 cm$^{-1}$, 567.3 cm$^{-1}$, and 742.3 cm$^{-1}$ are assigned as known Raman peeks for MoO$_2$ [4, 28, 42]. While the peak at about 380.5 cm$^{-1}$ originate from the E$^{1}_{2g}$ and at about 404.8 cm$^{-1}$ originates from A$_{1g}$ are the two primary peaks of MoS$_2$. Importantly, the energy separating these two phonon modes is 24.3 indicating that the MoS$_2$ in the nanoplates is about 3-5 layers thick [4, 14, 42, 43].
Figure 9: Raman spectroscopy of MoS$_2$ nanoplates indicating the MoO$_2$ and MoS$_2$, $E_{2g}^1$ and $A_{1g}$ peaks.
TEM is used to determine the crystallinity of the nanostructure. TEM image in Figure 10a shown a suspended nanoplate which is consistent with the SEM results. The selected area electron diffraction (SAED) pattern shown in Figure 10b indicates that the nanoplates have a crystalline structure.

Figure 10: a) TEM image of suspended vertical nanoplates. b) SAED pattern corresponding to the plate in (a).
4.2 Nanocrystals

At moderate sulfur condition, nanocrystal structures are grown. The mechanism of the nanocrystal formation can be explained in the following three-step reactions. In the first step, MoO$_3$ evaporates in molecular clusters. In the second step, the clusters condense on the substrate resulting in suboxide nanoparticles. During the third step, the nanoparticles are fully sulfurized to form nanocrystals [44]. The morphology of the nanocrystal structures is observed by SEM in Figure 11(a-b), confirming the size of the crystals between the range of 40 to 250 nm. Raman spectroscopy did not detect as much of the M – O vibration modes found in oxysulfide which was also previously reported by Liu et al., as a similar observation [38]. Also, since most of the nanocrystals have sizes about 200 to 400 nm which is smaller than the laser spots indicating that the laser could not focus enough to detect the MoO$_2$ signals. Additionally, Figure 12 shows the Raman spectrum for the nanocrystals and it clearly indicates the two vibrational modes of $E^{12g}$ and $A_{1g}$ peaks at 385.8 cm$^{-1}$ and 410.5 cm$^{-1}$ of MoS$_2$, respectively. Importantly, the energy difference between the two active modes was found to be 24.7 cm$^{-1}$ indicating that the MoS$_2$ in the nanocrystals is few layers thick [42, 45].
Figure 11: SEM images of as-synthesized nanocrystals.
Figure 12: Raman spectrum of MoS$_2$ nanocrystals indicating the MoO$_2$ and MoS$_2$, $E_{2g}^1$, and $A_{1g}$ peaks.
The layers of the MoS$_2$ shell are observed using transmission electron microscopy (TEM) as shown in Figure 13a, in which the layers appear at the outer surface of the nanocrystals and reveal a core-shell morphology. TEM characterization confirms the core-shell morphology of the MoS$_2$ nanocrystal. The cross-sectional high resolution TEM (HRTEM) image in Figure 13a shows the crystallinity of the crystal and high surface curvature structure which may contain exposed active edge sites. In addition, TEM analyses revealed that this nanocrystal has a size of 80 nm with 40 nm in diameter. HRTEM was used to identify the interlayer spacing between the sheet as seen in Figure 13c which was found to be 0.627 nm and agreed well with previous result [30]. The number of MoS$_2$ layers in the shell was identified from a magnified cross-sectional HRTEM image shown in Figure 13d which was found to be 8 layers and agrees with the Raman energy difference of the MoS$_2$ peaks. The high-angle annular dark field scanning TEM (HAADF-STEM) and Energy dispersive X-ray spectroscopy (EDS) mapping in Figure 14 confirmed an even distribution of Mo and S with a uniform distribution of O in the nanocrystals grown. This MoS$_2$ nanocrystal contains a high surface curvature thereby exposing more active edge sites.
Figure 13: TEM Characterization. (a) Cross-sectional HRTEM image of MoO$_2$/MoS$_2$ core shell. (b) TEM image of MoO$_2$/MoS$_2$ core shell. (c) Magnified cross-sectional HRTEM image of MoO$_2$/MoS$_2$ core shell showing layer spacing 0.627 nm and (d) number of layers.
Figure 14: HAADF-STEM and quantitative EDS mapping image verifies the MoS$_2$/MoO$_2$ core/shell nanocrystals. EDS mapping shows the chemical composition of oxygen at the center.
4.3 Triangles

MoS$_2$ growth experiments were carefully designed using MoO$_3$ thin film as the source of Mo. The substrate was coated with the seeding promoter, PTAS, to optimize the growth layer of MoS$_2$ [3,7]. Using MoO$_3$ thin film, uniform vapor pressure of Mo concentration was kept throughout the growth substrate. The introduction of sulfur was optimized by controlling the sulfur distance from the thin film. At 16.5 cm distance, sulfur evaporated at 620°C which was higher than the evaporation temperature of the thin film. This was to purposefully allow for nucleation of Mo to occur first then growth of MoS$_2$ as S vapor reached the environment at a flow rate of 10sccm and 750°C which was held for 5 minutes. The majority of the particles were triangular shaped as shown by the SEM images in Figure 14 (a-b).
Figure 15: SEM images of as-grown MoS$_2$ crystals
Figure 16: (a) Raman spectra for a MoS$_2$ single crystal. (b) PL single spectra of a MoS$_2$ crystal grown at the optimal growth condition.
Raman single spectra was obtained to confirm the layer number as well as the chemical composition of the material grown. As shown in Figure 16a, Raman spectrum has two prominent peaks which correspond to in-plane, $E_{2g}^1$, and out of plane, $A_{1g}$ vibrations of Mo and S atoms with Raman shifts of 384.8 cm$^{-1}$ and 405.1 cm$^{-1}$ respectively. The energy difference between these two peaks ($\Delta$) is 20.3 cm$^{-1}$ indicating few layers growth [30, 45-47]. Photoluminescence (PL) spectrum is shown in Figure 16b which is from a representative single crystal with peak intensity around 1.82 eV corresponds to direct band gap excitations.
CHAPTER 5: CONCLUSION

In conclusion, we introduced a new CVD method to synthesize 2D MoS$_2$ nanostructures using MoO$_3$ thin film as precursors. This new method enables uniform vapor pressure of Mo resulting of MoS$_2$ growth throughout the substrate and is highly reproducible. Diverse MoS$_2$ nanostructures including nanoplates, core-shell nanocrystals, and few layers MoS$_2$ crystals were synthesized using this method. Their structural and composition properties have been investigated using Raman, SEM, TEM, and PL spectroscopy. The results indicate that MoS$_2$ nanostructures assume specific morphology depending on the content of sulfur as the CVD environment changed from weakly to highly reduced during the growth process. This new CVD process can be used to synthesize other TMDCs materials on SiO$_2$ substrates as well as other type of substrates.

5.1 Future Perspective

The results of this work may have the potential contribution as electrocatalysts materials for hydrogen evolution reaction as well as materials for solar cell devices due to the conductivity property of MoO$_3$. Future investigation of those MoS$_2$ nanostructures may include their synthesis or transfer on conductive substrate for electrochemistry studies. Surface modification of those structures may also be investigated using bacteria for degradation studies as well as dyes for biosensing applications.
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