Development of Advanced 2D Membrane Materials for Shale Flowback Water Treatment

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By

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ABSTRACT

A model of design is provided in order to determine the most effective processes to fabricate and test a 2D Membrane for its effectiveness in water desalination. Water desalination with a 2D Membrane has already shown great theoretical results due to its energy efficiency that results from the thinness of the membrane. The 2D Membrane to be used in the model of design is Molybdenum Disulfide (MoS_2) due to its thickness of 3 atoms and Molybdenum's hydrophilicity. The need for water desalination is important, especially with the increased salt concentration in saline water. Current desalination plants cannot currently filter saline water. The process to be covered includes first fabricating the MoS_2 into 2D membranes (mono layered sheets), transferring the 2D sheets onto a predesigned suspension system, drilling a pore in the membrane in order to allow water to flow through, and setting up a forward osmosis process to evaluate the effectiveness of the membrane in desalinating saline water.

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1.0 INTRODUCTION

1.1 BACKGROUND

Throughout history, water has been vital for survival. Water can be used for many different things such as drinking, bathing, and producing power [3]. Every year, 2.4 million people die because of contaminated water [3]. Arsenic poisoning, caused by contaminated water, effects more than 20 million people in the Bengal region of India [3]. There are tons of other people in the world that are effected by contaminated water in many ways. These include multiple diseases and malnutrition due to a lack of proper hydration. The problem is usually in the supply of the water.

Although there is an abundance of water on earth (1.4*1021 Liters), more than 99% of is unavailable for use by humans. The amount of usable fresh water is only 0.7% of the total water available on earth. This is because seawater is not drinkable unless it is purified by the method of desalination [3], which is an energy-intensive process. Desalination used reverse osmosis to purify water because the water molecules are small enough to go through the membrane and the contaminant molecules are too large [3]. This filters the seawater and produces usable freshwater.

Water is also used for energy production. Over 40% of all water withdrawals are used for thermoelectric cooling [5]. The use of energy, especially with the ever increasing population, is always growing, so it is only natural that water withdrawals also increase in order to support energy production. Shale oil/gas is also a growing form of energy production.

Shale oil or gas is an unconventional fossil fuel resource. The production cost for shale oil is $23.35 per barrel as opposed to crude oil, which is $20.99 per barrel [5]. The energy is extracted by first drilling deep within the sub-surface. Water, sand, and chemicals, which are all combined to make fracking fluid, are then inserted into the earth in the drilled hole [6]. After the fracking fluid is inserted into the earth, it is then pumped out along with the natural gas. The natural gas is then extracted from the fluid and the fluid is returned to the surface [6] with both naturally existing and human-added constituents.

Given the hyper-saline flow back (returned or produced waters) water (> 190,000 ppm TDS, compared to ~ 35,000 ppm for seawater) and other chemical additives including benzene, toluene, ethylbenzene, and xylene with the possibility of naturally occurring radionuclides, treatment of flow back water for safe disposal and potential re-use is a challenging problem. In one study to determine whether a municipal waste water treatment plant (WWTP) could treat the flowback water [7] it was found that the effluent removed over 90% of the radium the high salinity with heavy metals such as barium and strontium caused significant increase in the fouling potential. Currently, the state of Pennsylvania limits incoming water stream to a WWTP to comprise no more than 3% of total water volume. The vast majority of flow back water is disposed without treatment through deep-well injection [8]. Out of the 3-5 million gallons of water needed per well for fracking, 20-40% of the fracking fluid flow back [27].

One promising use for treatment of such water is the use of nanotechnology. This is due to 2D membranes reduced hydraulic resistance and higher flux as compared to polymer membranes. Similar to the desalination process, nanostructured membranes made of carbon nanotubes, graphene, graphene oxide, zeolites, molybdenum disulfide (MoS_2), and boron nitride nanotubes are used in order to build novel, high flux reverse osmosis systems [3]. However, use of such materials for treatment of flow back water has never been considered. Specifically, this proposal will evaluate the feasibility of using molybdenum disulfide (MoS_2) as a potential membrane material to treat flow back water.

Although there are many 2D membranes, such as the ones previously stated, Molybdenum Disulfide (MoS_2) will be the membrane used in the study. MoS_2 has already shown great results for water desalination due to the high ion separation efficiency and it is also has a 70% increase in permeation rate than graphene [9]. A study was shown to determine the ion rejection efficiency using reverse osmosis and an applied pressure. Results show that the ion rejection efficiency for small pores (area of 36.16 $Å^2$) has an efficiency of 100% [9]. Results also show that larger pore areas (area of 55.45 $Å^2$) also have a high ion rejection efficiency of at least 90%, this efficiency depends on the applied hydrostatic pressure [9]. For instance, a MoS_2 nanopore with an area of 55.45 Angstrom squared and a hydrostatic pressure of 350 MPa has close to 90% ion rejection efficiency; on the other hand, a nanopore with the same area and a hydrostatic pressure of 250 MPa has an efficiency of around 95% [9]. In conclusion, the results from studies show that MoS_2 is a membrane that shows a lot of promise and more research still needs to be done to optimize on the efficiency and apply it on a real world scale.

1.2 MOTIVATION

Nearly all existing water treatment membranes are optimally designed for treating seawater with reverse osmosis and not shale flow water, which is 3-5 times saltier than shale water [10]. Currently, flowback water is disposed by deep well injections. Deep well injections can cause potential seismic activities. For instance, Oklahoma had a significance increase in earthquakes and this was due to the deep well injections as a way to dispose of the waste from oil and gas [8]. Oklahoma went from 50 earthquakes in 2007 to 6,521 earthquakes in 2016 [8].

The development of MoS_2 for water desalination is also important because it will drastically increase the efficiency needed to purify the water. Efficiency is a major problem in water desalination because a higher salt concertation results in more energy needed to purify the water [11]. As the water is purified, one side of the membrane because highly concentrated with salt, this means that even more energy is required to continue the desalination process [11]. MoS_2 is efficient due to its miniscule thickness of three atoms. Since efficiency is positively correlated with the thinness of the membrane used for water filtration, the results expected should result in an efficient filtration system.

1.3 CURRENT METHODS

The main method for water filtration is reverse osmosis. Reverse osmosis is a process in which pressure is applied on one side of a semi-permeable membrane containing salt water, as displayed in Figure 1 below.

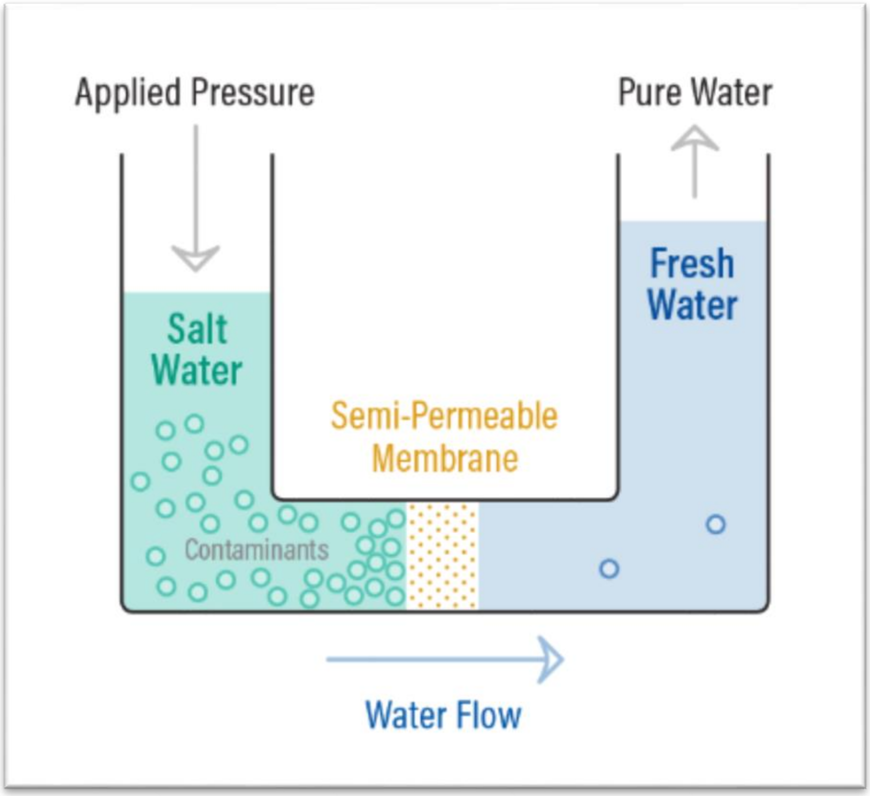

Figure 1: Reverse Osmosis through a Semi-Permeable Membrane [12]

Since water molecules are much smaller than salt molecules, the semi-permeable membrane is able to stop the salt molecules from getting through due to the size of the pores. The water flows from the salt water side to the fresh water side; after the process there should be a larger volume of water on the fresh water side than initially.

As stated in the previous section, the problem with water desalination comes from energy usage. In the reverse osmosis process, the energy usage comes from the applied pressure needed to move the water molecules through the semi-permeable membrane. The source of this applied pressure is usually a high pressure pump [13]. Energy usage in water desalination plants uses 200 million kilowatt-hours of pour each day, which constitutes for 55% of the total cost for desalination plants [14].

The semi-permeable membranes are used because they allow only certain molecules through. The membrane used is important because the water flux is inversely proportional to water flux. In essence, a thinner membrane equates to faster flow of water which uses less energy. Currently, most water desalination plants use polyamide films as the membrane [14]. However, MoS_2 is at least 1000 times thinner than the polyamide films [14]. This means that there is tremendous potential for the efficiency of water desalination with MoS_2 as the membrane.

1.4 OBJECTIVES

The goal of this research is to create a design model that will serve as a basis to effectively desalinate shale flowback water. The first step is to determine a method for making the 2D membrane form of MoS_2. MoS_2 exists in mainly a powder or bulk crystal form. The problem arises when attempting to obtain 2D form of the molecule. The 2D form of MoS_2 is a three atom thick membrane with a molybdenum atom in the center and two sulfur atoms on the outside. There are many complex methods into obtained the 2D form which include: chemical vapor deposition, liquid exfoliation, and mechanical exfoliation. These methods will be discussed in the later sections.

After determining how to make the 2D MoS_2 membranes, there needs to be a method to drill pores. The pores are important because they allow the flow of the water molecules through. The pores have to be a size in which they can let only the water molecules in and not the ions. The pore size should optimize on the water flux in order to improve efficiency.

Finally, with the pore drilled into the 2D MoS_2, the next step is to design and build a model for water flow. In order to simplify the research, this model should use forward osmosis so as to avoid applying pressure. Forward osmosis creates water flow when there is an osmotic pressure gradient between both sides of the membrane, as displayed in Figure 2 below.

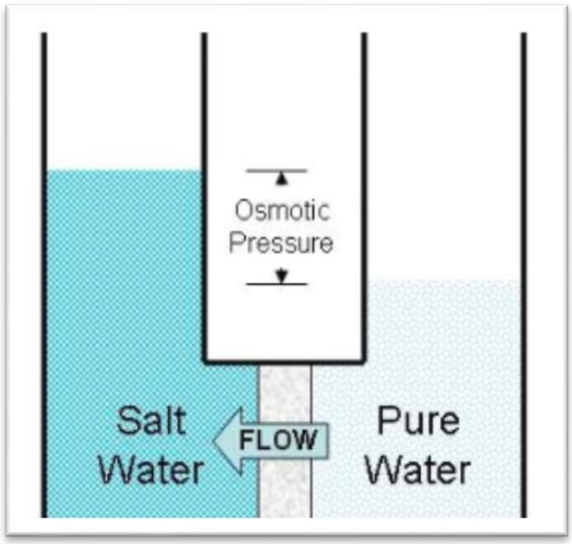

Figure 2: Forward Osmosis Diagram [15]

In this case, the water flows from the fresh water side to the salt water side. With the forward osmosis model built, the membrane effectiveness will be tested by evaluating the water flux.

2.0 SUPPORTING RESEARCH

2.1 GRAPHENE FOR WATER DESALINATION

There has been extensive research done on 2D membranes even before MoS_2 was discovered to be a good option for water desalination. Specifically, graphene was the main focus of the research. Graphene is a 2D membrane of carbon atoms that is one atom thick, unlike MoS_2, which is 3 atoms thick. The water desalination method for graphene is also reverse osmosis with a pore that allows the water to flow through the membrane. Figure 3 below displays the reverse osmosis process with a sheet of graphene as the 2D membrane.

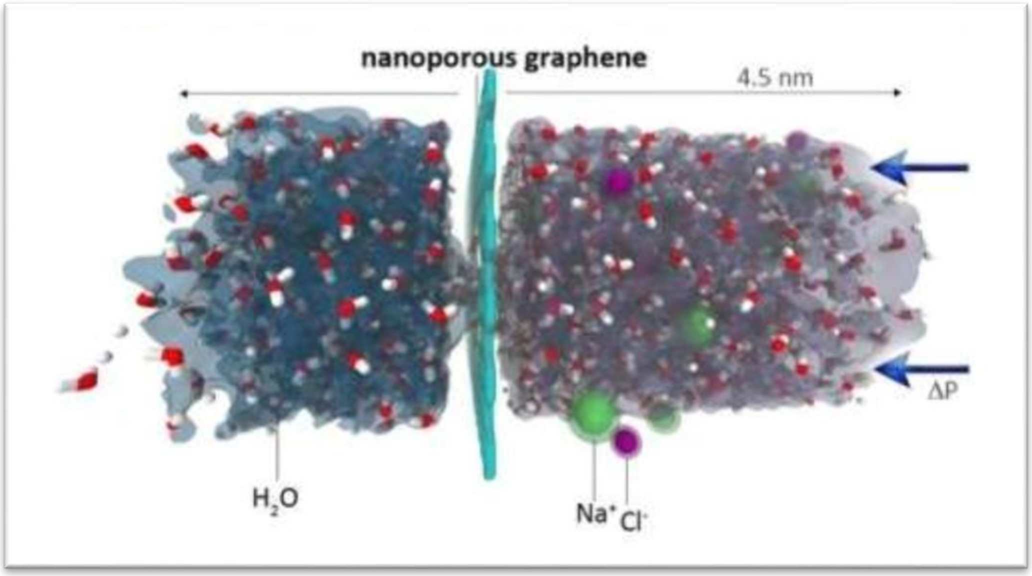

Figure 3: Reverse Osmosis with a 2D Graphene Membrane [18]

The pressure is applied on the right side of the membrane and only the water molecules (red and white) are allowed to go through the nonporous graphene, on the other side, the sodium and chlorine ions (green and purple) are left on the right side due to their side. Studies show that graphene uses 15% less energy to desalinate seawater and 50% less energy to desalinate brackish water than current desalination plants [16]. With all that in mind, MoS_2 was discovered to be 70% more efficient than graphene [17].

2.2 MOLYBDENUM DISULFIDE DYNAMIC SIMULATION

Molybdenum Disulfide showed promising results with dynamic simulations ran by The University of Illinois. These simulations ran a reverse osmosis set up with a rigid piston as the source for pressure as demonstrated in Figure 4.

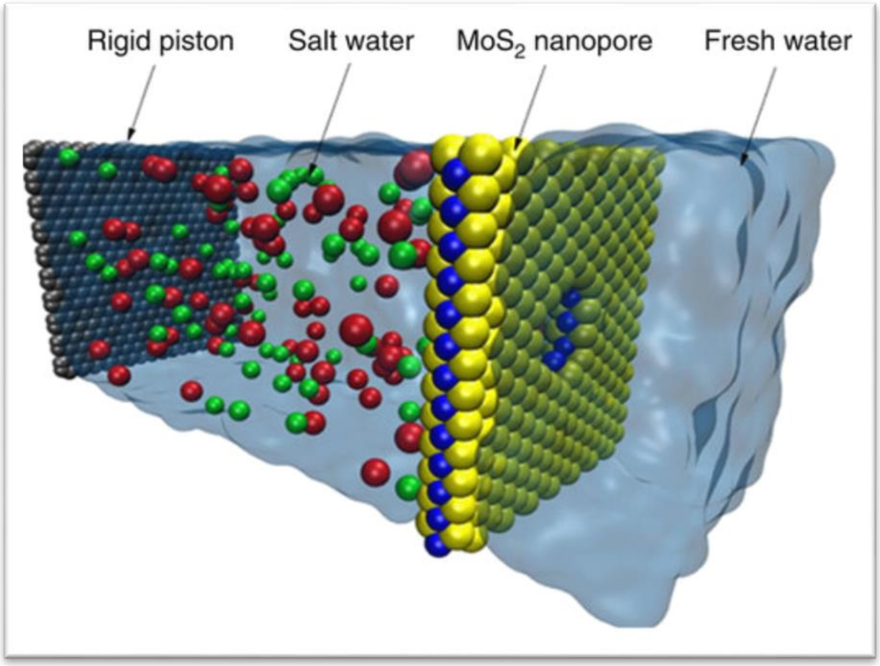

Figure 4: Diagram for MoS_2 used for Reverse Osmosis [9]

As explained before, the applied pressure pushes the water through the nanopore but rejects the ions. MoS_2 as a 2D membrane shows promising results because when a nanopore is formed there is molybdenum atoms around the edges of the pore [9]. Molybdenum is hydrophilic so it attracts the water molecules into the pore [9]. Since sulfur is hydrophobic, the water molecules are repelled towards the pore as the pressure is applied. When the water molecules go through the pore, they are repelled even more by the sulfur on the other side [9]. This results in a drastic increase in the water flux. There still needs to be more research on the ideal pore size to optimize water flux because when the area of the pore is 18.02 Å^2 there is 100% ion rejection efficient; however, when the area of the pore is 56.42 Å^2 there is around 90% efficiency [9]. For the same applied pressure from the rigid piston, the pore with the larger area has a larger water flux [9].

3.0 METHODOLOGY

3.1 FABRICATION OF 2D MOLYBDENUM DISULFIDE

3.1.1 CHEMICAL VAPOR DEPOSITION

The first method for fabricating 2D MoS_2 is chemical vapor deposition. Chemical vapor deposition (CVD) is a process used in industry to produce thin coatings onto substrates [19]. A quick diagram of the CVD process is displayed in Figure 5 below.

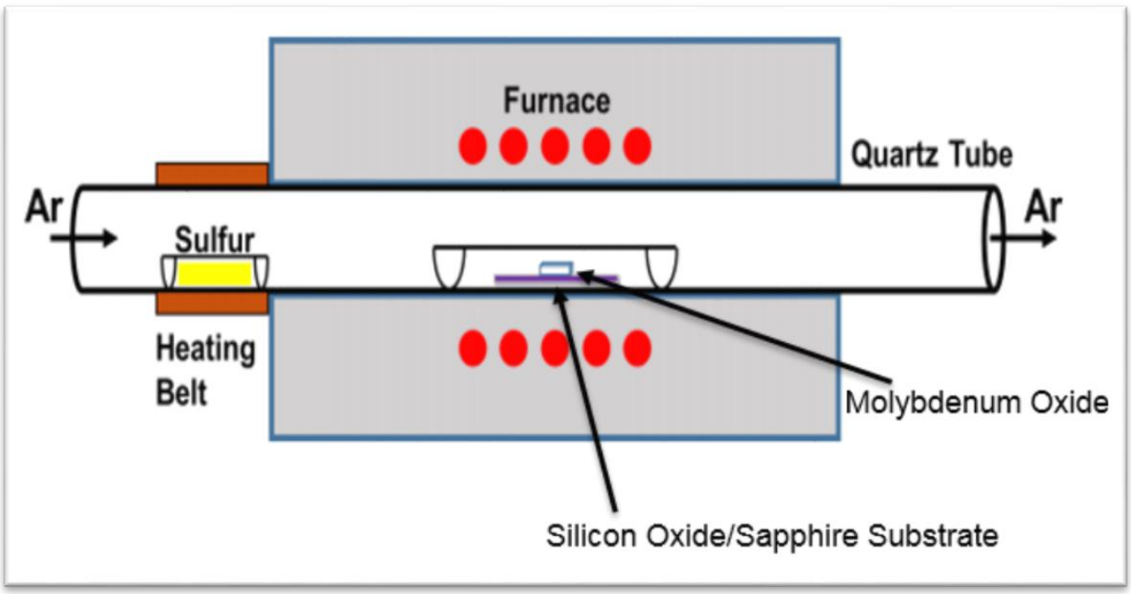

Figure 5: Chemical Vapor Deposition [20]

To make MoS_2, a Silicon Dioxide or Sapphire Substrate is covered with Molybdenum Oxide as a precursor to the chemical reaction as shown in Figure 5 [20]. The CVD furnace is then heated to 800°C with 100 sccm of Argon as the catalyst to speed up the chemical reaction [20]. The Sulfur, at the furnace entrance, is then heated by the heating belt to a temperature of 180°C and vaporized into the furnace. The sulfur undergoes a chemical reaction with the molybdenum oxide and the argon as a catalyst to produce a 2D flakes of mono-layered MoS_2 on the substrate.

CVD is an efficient method to fabricate 2D MoS_2, however there are some negatives that come along with the process. Due to the high temperatures needed for CVD, the energy requirements are substantial. Using a CVD furnace also takes an expert who has sufficient experience. Fortunately, there is a CVD available at the NanoSystems Laboratory at The Ohio State University for a rate of $10 per hour.

3.1.2 LIQUID EXFOLIATION

Another method of 2D MoS_2 fabrication is liquid exfoliation. Liquid exfoliation is a method to obtain thin layers of nanosheets. The process begins by sonicating MoS_2 with N-methyl-pyrrolidone (NMP) as the solvent [21]. After the sonication, the solution is centrifuged in order to obtain dispersions [21]. This dispersion contains mono and multi-layer MoS_2. Transmission Electron Microscopy can be used to analyze the different layers of the MoS_2. Vacuum filtration is then used to prepare the 2D flakes that will then be deposited onto the substrate by spraying [21].

Fortunately, liquid exfoliation does not require extensive use of complicated equipment. However, the MoS_2 sheets that are fabricated are not all mono-layered. For further analysis Scanning Electron Microscopy and Atomic Force Microscopy can be used.

3.1.3 MECHANICAL EXFOLIATION

Mechanical Exfoliation is the last fabrication method to be discussed. The process is relatively easy as compared to the others. As opposed to MoS_2 in its powdered form, for mechanical exfoliation the MoS_2 has to be in bulk crystal form. The process starts by placing the bulk crystals onto scotch tape [22]. Then the scotch tape is used to peel the crystal until it appears less dense [22]. The amount of times the scotch tape needs to be separated is arbitrary, but anywhere from four to eight times is okay. The thin crystals are then deposited onto a SiO_2 or a sapphire substrate by simply placing the tape on the substrate[22]. A plastic tweezer is then used to rub the tape in order to further cleave the MoS_2 [22]. Optical and atomic force microscopy can be used to characterize the layers as shown in Figure 6.

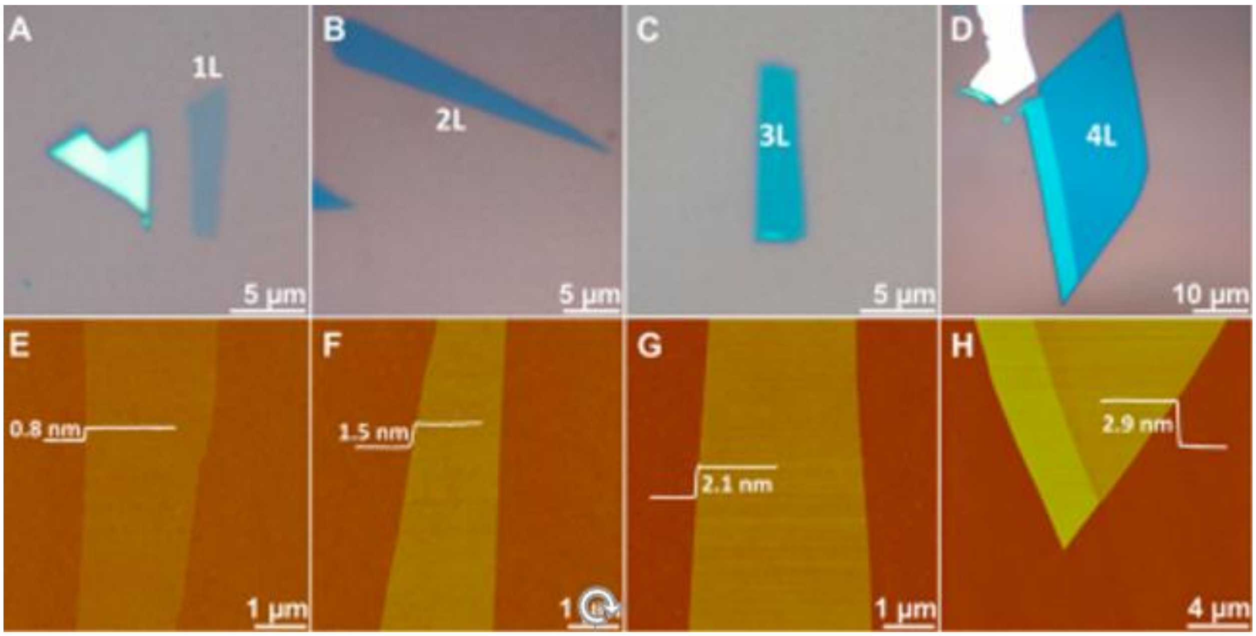

Figure 6: Optical and Atomic Force Microscopy Images of Mechanically Exfoliated MoS_2 [22]

Figure 6 shows a picture of both optical microscopy (A-D at the top) and atomic force microscopy (E-H at the bottom). To ensure the right chemical makeup is fabricated, a raman verification can be used to test the sheets of MoS_2. The raman characteristic measured has to match the plot shown in Figure 7 below.

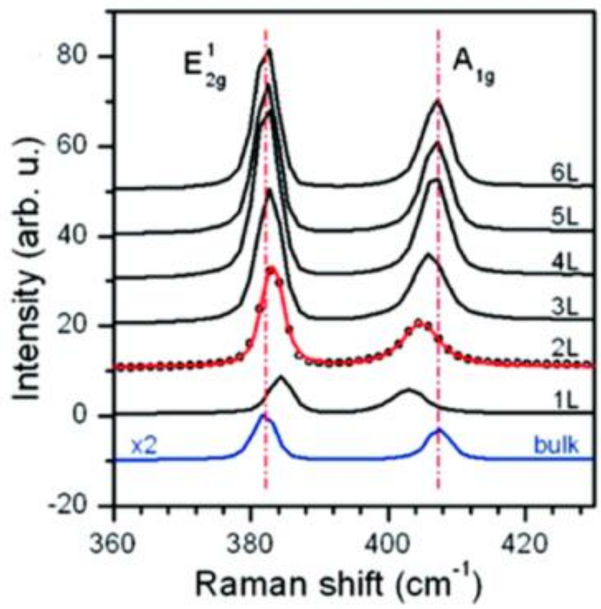

Figure 7: Raman Characteristics of 1-6 layered MoS_2 [22]

Unfortunately, with mechanical exfoliation there are multilayered sheets of MoS_2. The most common layers are between 1 and 15 [22]. However, with optical imaging and ImageJ, it is easy to determine the amount of MoS_2 layers on a given area of the substrate [22]. Table 1 below gives a summary of the pros and cons of each method.

Table 1: Different Methods to Fabricate 2D MoS_2

Chemical Vapor Deposition	**Pros**	**Cons**
	Single Layered 2D Flakes produced	High energy due to high required temperature
	Easy to scale up to large scale production	Expert level required for CVD furnace
	CVD is a commonly used process in industry	Tedious for small scale usage
Liquid Exfoliation	**Pros**	**Cons**
	Cheap Process	Expert level required for chemical processes
	Equipment required is readily available	Mono layared and Multilayered 2D Membranes are produced
Mechanical Exfoliation	**Pros**	**Cons**
	Easy method	Produces a large variety of layers
	No complex material required	

3.2 TRANSFER OF MOLYBDENUM DISULFIDE FROM THE SUBSTRATE

3.2.1 POTASSIUM OXIDE ETCHING

Before a pore is drilled onto the MoS_2, there needs to be a suspension for the membrane so it can be free standing and permit the flow of water. The suspension is made of a Silicon Dioxide membrane with CVD grown Silicon Nitride on each side [23]. Potassium hydroxide will be used to etch (chemical milling) the Silicon Dioxide and Silicon Nitride while leaving one of the Silicon Nitrides on either side untouched as displayed in Figure 8 [23].

Figure 8: Suspension System after KOH Etching [23]

The pink and blue represents Silicon Nitride in Figure 8. The etching process is aborted before making a through hole because the hole created would be too large to mount the MoS_2. The next step is to make a smaller hole in the Silicon Nitride, the top pink line in Figure 8. This is done with electron beam (e-beam) lithography and reactive-ion etching (RIE), a more precise form of chemical milling [23]. The target size of the hole is 200 to 500 nanometers. Figure 9 displays the suspension system after electron beam lithography and reactive-ion etching.

Figure 9: Suspension System after E-Beam Lithography and RIE [24]

With the hole made, the MoS_2 flake is ready for transferred onto the suspension.

3.2.2 POLYMER TRANSFER METHOD WITH POLY(METHYL METHACRYLATE)

The polymer method is used to transfer thin films onto substrates. The goal of this method is to transfer the MoS_2 from the sapphire or silicon dioxide substrate onto the suspension system. This method starts by first spin coating Poly(methyl methacrylate) (PMMA) onto the substrate [24]. This binds the MoS_2 and PMMA together. Then the substrate, along with MoS_2 and PMMA, are placed into a beaker of water for ultrasonic cleaning [24]. The PMMA and MoS_2 float to the top because of the ultrasonic treatment and are separated from the substrate. The film is then deposited onto the suspension system. After the deposit of the film, acetone is used to dissolve the PMMA [24].

3.3 METHOD TO DRILL PORE INTO MEMBRANE

3.3.1 TRANSMISSION ELECTRON MICSROCOPY METHOD

The first method to drill the pore is with the Transmission Electron Microscope (TEM). TEM method consists of emitting a beam of electrons onto the suspended monolayer MoS_2. The first step in this process is to determine whether the MoS_2 was successfully transferred onto the hole [23]. This can be done with a low magnification TEM imaging to determine whether the MoS_2 is under the correct shade of light [23]. When the intensity is increased, the TEM can drill a hole into the MoS_2 sheet. The size of the pore can be measured by using TEM imaging. Although the TEM method is fairly simple, it is difficult to be precise, especially with the pore size needed (around 5Å).

3.3.2 ELECTROCHEMICAL REACTION METHOD

Another method to drill a pore into the MoS_2 is with an electrochemical reaction. The way it works is by applying a potential difference across the membrane until a current is measured [25]. First, the membrane is put in a microfluidic flow-cell with an aqueous buffer [25]. Then a potential difference is applied with Ag/AgCl electrodes. The potential difference is slowly increased until current is detected, as shown in Figure 10.

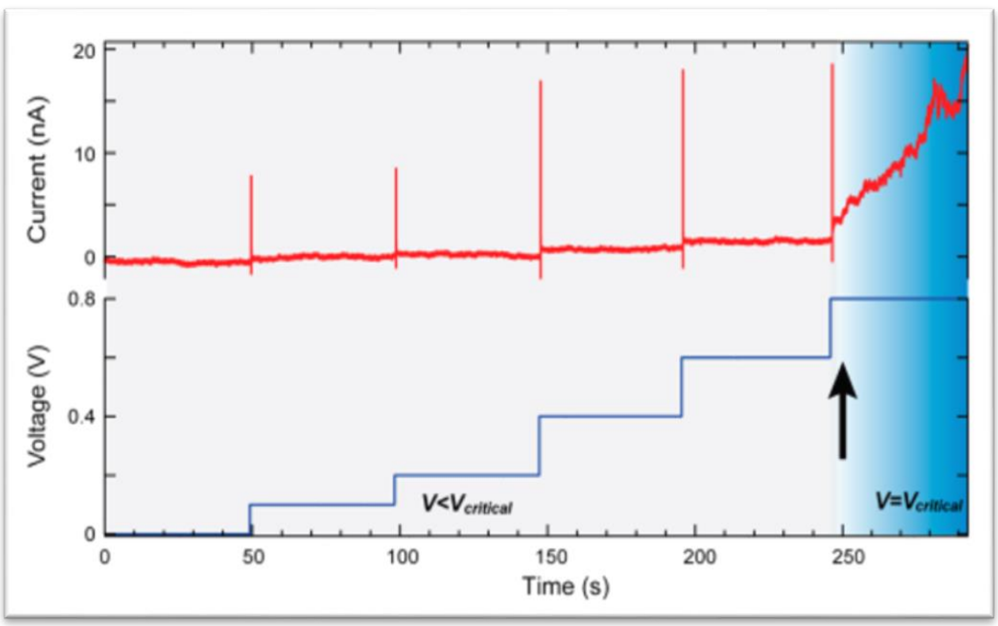

Figure 10: Ionic Current across MoS_2 with respect to Voltage Increase [25]

The pore is formed when the current begins to flow. An increase in current value correlates with an increase in pore size. This method is more efficient that TEM drilling because the pore size can be easily controlled depending on the applied potential difference and measured current. Table 2 below gives a summary of both methods used to drill pores.

Table 2: Methodology to Drill Pores into MoS_2 2D Membrane

TEM Drilling	**Pros**	**Cons**
	Relatively quick method	Inefficient when controlling pore diameters under 1 nanometer
	Easy experimental setup	
	TEM is readily available	
Electrochemical Reaction	**Pros**	**Cons**
	Easy to control pore size	Extensive experiment setup
	Pore size is linked to measured current	Materials required to induce potential difference and current

3.4 MODEL FOR WATER FLOW

The flow set up to determine is similar to the set up to fabricate the pore in the membrane. There will be saline water on one side on the water and clean or fresh water on the other side as displayed in Figure 11.

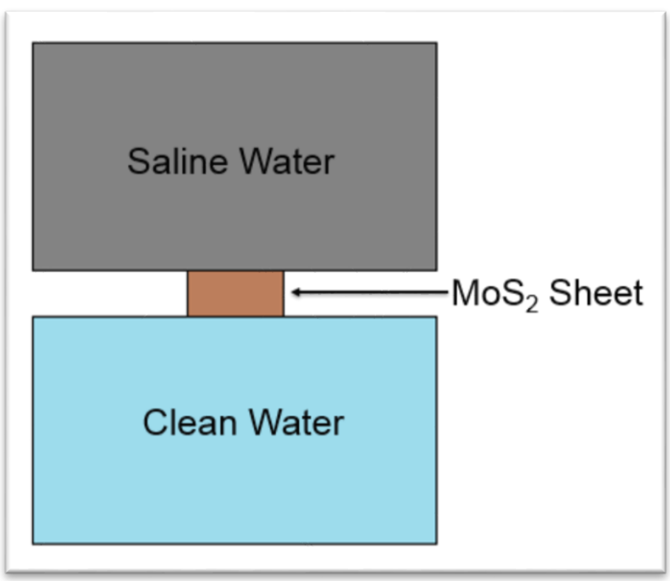

Figure 11: Flow Set Up for Water Desalination

The potential difference and induce water flow will be measured to determine the effectiveness of the membrane. For ease of experimental set up, this experiment will be forward osmosis, unlike the traditional means of water desalination. As previously explained, the forward the water will flow from clean to saline. Another check to determine the effectiveness of the membrane is to determine whether the salt concentration increases in the clean water. The concentration of the salt in highly saline water is from 10,000 to 35,000 ppm. With the desalination, the goal is to obtain the concentration of sea water, which has a salt concertation less than 1,000 ppm [26].

4.0 CONCLUSION

4.1 FUTURE WORK

Although a lot of the ground work has been done on using the fabrication and use of MoS2 as a membrane for water desalination, there is still a lot to be done. The first step is to determine the most efficient method to produce single layer of MoS2. I believe mechanical exfoliation should be used initially, even though it is not the most efficient method. Mechanical exfoliation the cheapest method because minimal equipment is required for the process. Another step is to determine the method to drill the pores into the membrane. Using an electrochemical proves to be the best way because it is easier to control the pore size than the TEM drilling way. As well as determining the method to fabricate and drill pores into MoS_2, there needs to be a more concrete set up for the water flow. Essentially, the components required for the water flow set up need to be determined.

4.2 SUMMARY

MoS_2 as a membrane for water desalination has already shown tremendous potential. If the future experiments shows good results there needs to be a lot more done to scale up. Industries have to determine the most efficient and cost effective way to fabricate the 2D membranes. For a large scale production, CVD is most likely the best way to fabricate the 2D membranes due to the availability of CVD furnaces in industry. Mechanical exfoliation on a large scale production would be too tedious and inefficient. They also have to determine the best way to drill pores in the membranes and the water flow set up for the desalination process. Electrochemical reactions would still be the most ideal under large scale production. There are currently no large scale facilities that produce MoS_2 2D membranes.

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