TWO-DIMENSIONAL NANOPORE AND NANOPOROUS DEVICES FOR MOLECULAR SENSING AND ION SELECTIVITY

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A DISSERTATION

in

Electrical and Systems Engineering

Presented to the Faculties of the University of Pennsylvania

in

Partial Fulfillment of the Requirements for the

Degree of Doctor of Philosophy

2018

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Acknowledgments

I would like to first and foremost thank my advisor and mentor Dr. Marija Drndić for all the support and belief she had in me, and who taught me to look for the silver lining in all kinds of situations. I hope to be retain my optimism throughout my life which she inspired in me. I would also like to extend my thanks to my dissertation committee, Dr. A T Charlie Johnson, Dr. Cherie R Kagan and Dr. Alison Sweeney, for their helpful suggestions, comments and encouragement throughout my dissertation.

I want to express my thanks to my labmates at the Drndić lab, who have been more like a family to me. In particular, Paul Masih Das, for being a brilliant collaborator and an equally awesome friend, and who would be a constant positive driving force from the ideation through the execution to the publication phase of all our projects together; Yung-Chien Killian Chou and Jothi Priyanka Thiruraman, with whom I could bounce around and experiment with ideas both scientific and philosophical, no matter how random and crazy; Jerome T Mlack, with whom I could discuss interesting projects, and get help with exploring and understanding my data even though it had nothing to do with his own projects; David Niedzwiecki, who would always give me a patient ear, encouraging words and insightful thoughts, be it about science experiments or life experiences; William Parkin, for coding those extremely useful analysis software which made extracting useful statistics from terabytes of data feel like child's play; Chien Francis Chen-Chi, for helping me out with fabrication, measurement and analysis of devices, always with a smile; Sarah, on whom I could always trust to give me an honest opinion, however brutal it might be; Kimberly Venta, Matt Puster, Julio A Rodriguez Manzo, Adrian Balan, and Jae-Hyuk Ahn for mentoring me and being patient with me when I was just starting out in the lab. I would also like to thank my collaborators at Penn, Penn State, RPI, and ICB France, including Dr. A T Charlie Johnson, Dr. Mauricio Terrones, Dr. Vincent Meunier and Dr. Patrick Senet, and their group members, Carl Naylor, Kazunori Fujisawa, Andrew Cupo and Adrien Nicolaï for their invaluable insights and inputs.

I would like to gratefully acknowledge Dr. Douglas Yates, Dr. Jamie Ford, Dr. Matthew Brukman, Eric Johnston and Dr. Gerald Lopez for their help with sample preparation, characterization and cleanroom instrument training at the Singh Center for Nanotechnology, University of Pennsylvania, Dr. Robert Keyse at Center for Advanced Materials and Nanotechnology, Lehigh University for his assistance with AC-STEM measurements, and David Hopper for his valuable help in designing optical experiments.

I am deeply indebted to my Philly family of friends who helped me keep sane throughout my journey here. I would like to specially thank Sravya Kotaru for being a patient listener, a dependable roommate, an insightful critic and a true friend; Rajatesh Gudibande for being a positive and encouraging force in my life; Aditya Narayan, Utsav Mehta, Aryan Thaker, Nirav Shah, Falguni Shah, Prashanth Rangarajan, Tharun Reddy, Udit Mathur, Aayush Sharma, Siddharth Saxena, Arvind Subramanian, Sukreeti Sehrawat, Badrinath Rayadurg, Akshay Vijaygopal, Vinay Cherku, Neeraja Reddy, Sagar Hoskeri, Deepika, Anisha Gadikar for being an integral part of my PhD life on whom I could count on no matter the situation.

And finally, I would like to thank my family - my parents Dr. Tarun Kumar Danda and Dr. Sharmila Danda Pal, for their selfless love, support and blessings without which I wouldn't be here today, my sister Debopriya Danda for her tireless guidance and encouragement, and my soulmate and wife, Neema Kumari. Neema: thank you for being my bedrock, for your trust in me, and, most of all, for proving that love can conquer all - thank you for everything.

ABSTRACT

TWO-DIMENSIONAL NANOPORE AND NANOPOROUS DEVICES FOR MOLECULAR SENSING AND ION SELECTIVITY

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Nanopore-based devices provide the ability to detect, analyze and manipulate molecules by monitoring changes in ionic current and sieving molecules dissolved in an electrolyte. While devices with single nanopores can be used as molecular sensors and analyzers, including as a possible high-throughput DNA sequencer, devices with multiple nanopores (nanoporous devices) can be used to filter out ions from solutions, with possible use in water desalination. Sensitivity and molecular flux can be enhanced by using two-dimensional (2D) materials, like graphene and transition metal dichalcogenides (TMDs), as the nanopore membrane. However, these devices face challenges yet to be solved, including (a) fast DNA translocation velocity through 2D nanopores that limits temporal resolution required to achieve DNA sequencing, and (b) sensitive fabrication techniques that prevents large-scale commercialization of such devices. Additionally, TMD nanoporous membranes have been predicted to possess higher permeability of water molecules than their graphene counterparts, but no related experiments have been presented. In this dissertation, we explore not only ways to tackle the stated limitations, but also perform ion selectivity measurements through ion-irradiated TMD nanoporous devices.

First, we investigate ionic flow and associated leakage currents in voltage-gated graphene nanopores predicted to help slow down DNA translocation velocity. We extract important parameters that can help reduce leakage currents while enhancing the signal strength and gating control.

Next, we report DNA detection with high sensitivity through monolayer tungsten disulfide (WS₂) nanopores fabricated via electron-beam drilling and observe laser irradiation induced expansion of the pore, which we are able to control with nanometer precision. Follow-up experiments are performed, wherein we characterize this technique by irradiating intact suspended WS₂ membranes to fabricate nanoporous membranes and measure dependence of the induced defect sizes and density on laser power density. This process can be fine-tuned in future studies to enable facile creation of both nanopores and nanoporous devices based on TMDs.

Additionally, we study and calibrate sub-nm defect formation in suspended molybdenum disulfide membranes using ion-beam irradiation. Ionic current characterization of the devices exhibits selective ionic transport, thus laying experimental foundation for future studies on TMD-based nanoporous devices for water desalination.

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Chapter 1

Introduction

1.1 Motivation

Atomically-thin two-dimensional (2D) materials have been studied since 1940s, [177] but the first isolation of such a nanomaterial - graphene, which is a single layer of carbon atoms arranged in a benzene-ring structure - was demonstrated by Novoselov *et al.* in 2004. [131] This discovery led to renewed interest in these novel nanomaterials eventually giving rise to further isolation and investigation of a family of 2D materials (transition metal dichalcogenides or TMDs, boron nitride, phosphorene, etc.) and development of devices based on these materials. Low dimensionality of 2D materials results in unique effects which are otherwise not seen in their bulk counterparts - like band splitting due to quantum confinement, [114, 156, 187] ballistic electronic transport (in graphene), [44, 116] band gap transitions (in TMDs like MoS_2 , WS_2 , etc.), [45, 114, 145] and increased strength and flexibility [4, 76, 90] among others.

Such improvements in electrical, mechanical and chemical properties of 2D materials over bulk forms have led to their utilization in a range of applications including batteries and supercapacitors, [102, 141, 198] field effect transistors (FETs), [20, 36, 97, 100, 131, 154] flexible and transparent electronics, [7, 20, 74, 77, 89, 180] solar cells and photodetectors, [60, 166, 171] catalysts, [5, 21, 170, 197] molecular sensors, [34, 55, 56, 103, 105, 121, 152, 209] and filtration devices. [26, 69, 133, 134, 147, 165, 168, 204]

In our work, we utilize the atomic thickness and ionic impermeability of 2D sheets to make transmembrane devices, [55] which can be modified to contain nanoscale defects allowing only molecules of specific sizes to pass through, creating molecular sensors [34, 121] and filters. [168] Using such atomically-thin 2D materials can provide advantages over prevalent thicker 3D membrane materials such as stronger signals for molecular detection [56] and larger flux for filtration purposes. [26]

In the following subsections, I will provide a brief introduction to the concepts of nanopore sensors and nanoporous filters and the advantages of using 2D materials in these devices, before moving to specific details of experiments and results in the following chapters.

1.2 Nanopore Sensors

The concept of nanopore sensors is based on Coulter counters, [32] where a thin membrane with a single pore in it divides two reservoirs of ionic electrolytes. When a voltage is applied to the electrolyte across the membrane, ions flow through the pore constituting an ionic current. If a charged particle, smaller than the size of the pore, is introduced in the solution, it can be driven through the pore due to the electric field across it. As the particle passes through or translocates through the pore, it will reduce (or in some cases enhance) the ionic concentration inside the pore, resulting in a change in the ionic current (referred to as a translocation event), which is dependent on the size and charge density of the particle. Usually Coulter counter pores are in the micrometer regime and finds use in counting cells and other micrometer-size particles. However, if these pores are fabricated in the nanometer regime, they can be used to detect and analyze sub-micrometer molecules, including biomolecules. Device schematic of such a nanopore device based on graphene and the corresponding DNA translocation events are shown in Figure 1.1. [121] One of the most common application of nanopore sensors is in DNA sequencing. [39, 126, 173]



Figure 1.1: Left: Device schematic of a few-layer graphene (1-5 nm thick) suspended over a 1 μ m diameter hole in a 40 nm thick silicon nitride (SiN) membrane. Right: Time traces of ionic current showing DNA translocations for a 7.5 nm nanopore with 1 nM 15 kbp dsDNA at 100 mV applied bias, with the corresponding TEM image of the nanopore on the bottom left and concatenated sequence of sample events on the bottom right. Adapted with permission from [121]. Copyright 2010 American Chemical Society.

Nanopore sensors should be able to sequence single stranded DNA by discrimi-

nating its four nucleotides (adenine, thymine, guanine, cytosine) due to their subnanometer size difference which would result in different levels of ionic current blockage. [47, 175] In fact, protein nanopores like α -hemolysin [25, 72] and MspA [41] have been shown to successfully detect and sequence DNA. However, use of such nanopores and associated membranes and enzymes require specific restrictive conditions to be fulfilled like ionic concentration, temperature, solution pH values, and so on, to function properly, and provide no control over nanopore size, [40] making large scale commercialization and integration with current electronics difficult. This motivated the development of solid-state nanopores.

1.2.1 Solid-State Nanopore Sensors

Solid-state nanopore sensors are generally based on silicon-based membranes like silicon nitride, [94] silicon oxide [163] and amorphous silicon. [146] Lithographic techniques common in the semiconductor industry can be adapted with relative ease to fabricate suspended silicon membranes, in which nanopores can be drilled with nanometer precision either using a focused electron beam [163] or using the recently developed voltage-induced breakdown. [191] This enables the use of such sensors not only for DNA sequencing applications, but also for detection and analysis of molecules with variety of sizes and structures like RNA [183] and gold nanoparticles. [176] Surface modification can also be performed to further customize the sensors for specific purposes. [184]

While solid-state nanopores, when compared to their protein counterparts, are relatively more robust to chemical and mechanical conditions, provides more control over nanopore dimensions and can be integrated with ease to existing semiconductor technologies, they have their own drawbacks:

- Spatial Resolution Limit Silicon-based pores are unstable below 1 nm thickness. [146] As the DNA nucleotides are thinner in comparison (~ 0.3 nm), during DNA translocation there would be at least 3 consecutive nucleotides inside a 1 nm pore at a single time thereby requiring discrimination of at least C(4, 3) $= \frac{(3+4-1)!}{3!(4-1)!} = 20$ different ionic current levels (allowing for base repetition), and even then the nucleotides can be differently ordered for the same signal (*i.e.*, {ATG} would give the same current drop as {AGT}, {TAG}, {TGA}, {GAT} or {GTA} resulting in a total of P(4, 3) - C(4, 3) = 4³ - 20 = 44 undetected combinations).
- **Temporal Resolution Limit** DNA translocates extremely fast ($\sim 30 \times 10^6 \text{ nt/s}$) [51] and current electronics is not fast enough to detect signals at that frequency (*i.e.*, 30 MHz). It would require either high bandwidth, low noise signal detection electronics [155] or manipulation of DNA velocity to get the required temporal resolution for single-base discrimination.

Some of these discussed problems can be mitigated, if not eliminated, by the use of 2D materials.

1.2.2 2D Nanopore Sensors

The ionic conductance of the pore is inversely proportional to the thickness of the membrane as given by:

$$G = \frac{I}{V} = \sigma \left(\frac{4L}{\pi d^2} + \frac{1}{d}\right)^{-1} \tag{1.1}$$

where G is the conductance of the nanopore, I is the ionic current signal, V is the applied voltage, σ is the electrolyte conductivity, L is the membrane thickness and d is the diameter of the pore. This would mean a thinner membrane will give rise to a stronger signal. Atomically-thin 2D nanopores can as a result provide the maximum available signal owing to the minimum thickness of a single atom. In fact, the equation becomes simpler for 2D materials as the first term becomes negligibly small and the signal becomes dependent only on the nanopore diameter and the electrolyte concentration:

$$G = \sigma d \tag{1.2}$$

For the purpose of DNA sequencing, single base resolution is also predicted to be possible by using 2D materials, as the thickness of such nanopores approach that of a single base thickness (thickness of graphene ~ 0.3 nm).

Limitations of 2D nanopore sensors

2D nanopores have been demonstrated not only to detect DNA translocations [34, 55, 56, 103, 105, 121, 152, 209] but also to differentiate between different nucleotides. [47] However, to achieve DNA sequencing, the temporal resolution limit still needs to be solved, as the DNA velocity through 2D materials is comparable to that of silicon nanopores ($\sim 20\text{-}100 \times 10^6 \text{ nt/s}$ [34, 56, 103, 105, 121, 152, 209]) as shown in



Figure 1.2: (a) Translocation velocity of 15 kbp dsDNA as a function on applied voltage bias through graphene nanopores. Adapted with permission from [121]. Copyright 2010 American Chemical Society. (b) Scatter plot of translocation events of 48 kbp λ -DNA through molybdenum disulfide (MoS₂) nanopores. Adapted with permission from [103]. Copyright 2014 American Chemical Society. (c) Translocation event length for 10 kbp dsDNA as a function of applied voltage bias through boron nitride (BN) and silicon nitride (SiN_x) nanopores. Adapted with permission from [105]. Copyright 2013 John Wiley and Sons.

Figure 1.2. While there is ongoing research to enable high bandwidth amplifiers, [148, 155] slowing down of DNA is also being considered by utilizing pressure, [200] temperature, [12, 51, 193] light [42] and voltage [174] as controls.

Another limitation of solid-state nanopores is the use of focused electron beam, specifically, transmission electron microscopy (TEM), to drill nanopores (Figure 1.3a), [163] which makes large-scale production of nanopore devices difficult. Recently, voltage-induced breakdown of dielectric membranes [86, 191] has been shown to form nanopores (Figure 1.3b) but the location of which is hard to predict. Voltage-induced electrochemical reaction of 2D membranes have also shown a similar effect [49] although the underlying mechanism is not yet well understood.

TMD membranes are also known to be electrochemically active under laser illumination. [6, 19, 53, 111, 136] This property can possibly be engineered to not only



Figure 1.3: (a) Schematic of electron beam drilling of nanopores (top) and TEM image of an e-beam drilled ~ 10 nm silicon nanopore (bottom). Adapted with permission from [163]. Copyright 2003 Springer Nature. (b) Voltage-induced dielectric breakdown of SiN to fabricate nanopores (1-4), leakage current densities with varying electric field (bottom-left), and ionic current monitoring during nanopore fabrication (bottom-right). Adapted from [86].

fabricate nanopores in suspended TMD membranes but also to control their sizes. Laser-induced damage and how to prevent such damage to preserve its optoelectronic properties [2] have been studied in literature, but there has been no study on how to control such damage and use it for nanopore applications.

In **Chapter 3**, we explore the above two limitations of 2D material-based nanopore sensors in detail. Particularly, we study graphene nanopores and analyze leakage current associated with voltage application to such nanopores necessary for voltageinduced DNA velocity control. We also investigate the use of monolayer tungsten disulfide (WS_2) nanopore sensors for DNA detection and the effect of laserillumination on the nanopores in solution.

1.3 Nanoporous Membranes

Reverse osmosis (RO) is the most common method of desalinating water currently. It involves transport of water molecules through the gaps in a porous media (usually made up of a polymeric matrix) by applying high pressure, while filtering out hydrated salt ions by the small size of gaps (0.3-0.6 nm) in the matrix. [138] For a RO membrane, optimization of the following properties is important:

- **Permeability** High rate of water transport through the membranes or permeability would result in faster filtration. For polymeric membranes, as the water molecules have to travel through a micrometer-thick matrix, the permeability tends to be quite low (< 1 L/cm²/day/MPa). [1] This results in much high driving pressure requirement when compared to other filtration techniques (like nanofiltration, ultrafiltration, etc.), which in turn results in relatively higher energy usage. [172]
- **Selectivity or Rejection Ratio** Membranes need to be highly selective (*i.e.*, can get rid of most of the dissolved salt) to enable high quality filtration. The rejection ratio (R) is given by [172]:

$$R = 1 - \frac{c_p}{c_f} \tag{1.3}$$

where c_p is the permeate (or collected water) ionic concentration and c_f is the feed ionic concentration. This is determined by the average pore size of the membrane which needs to be < 0.7 nm to prevent hydrated salt ions from passing through while allowing passage of water molecules unhindered (diameter of water molecule ~ 0.6 nm). [26, 28]

Mechanical Stability The membranes need to be able to withstand high pressures (0.5-12 MPa) associated with the RO process. [172]

On top of these factors, cost and efficiency are also important aspects to consider as they can limit large-scale adoption of the technology.

1.3.1 2D Nanoporous Membranes

2D materials have grown in popularity as possible RO membranes as they provide advantages over traditional membranes. Due to their atomic thickness, the water permeability for such membranes is expected to be high (> $10 \text{ L/cm}^2/\text{day/MPa}$). [26] 2D membranes are also known to possess very high mechanical strength, graphene being the strongest material reported yet. [14, 27, 90, 104] Techniques have been developed to introduce sub-nm defects in intact 2D membranes using ion irradiation [92, 109, 132] and chemical or plasma etching. [79, 133, 179, 188] All of these factors, coupled with reproducible CVD growth techniques and large-scale transfer procedures of 2D materials, [7, 75, 77, 97] have given rise to intense research in this field in recent years.

Graphene membranes have been studied as desalination membranes both the-



Figure 1.4: (a) Molecular dynamics (MD) simulation of water desalination through graphene nanoporous membranes. Adapted with permission from [26]. Copyright 2012 American Chemical Society. (b) Experimental study of ion selectivity of graphene nanoporous membranes fabricated using ion-beam irradiation and subsequent oxidative etching. Adapted with permission from [132]. Copyright 2014 American Chemical Society.

oretically and experimentally (Figure 1.4). It has been predicted using molecular dynamics studies that pore size and functional group termination of defects affect both permeability and ion selectivity, showing a minimum pore diameter of ~ 0.4 nm to effectively block hydrated salt ions (K⁺, Na⁺, Cl⁻), [204] while functionalized negatively charged pore diameters of ~ 0.5-0.7 nm to selectively allow K⁺ ions compared to Na⁺ and Cl⁻ ions. [26, 158, 204] Ion selectivity have been demonstrated for graphene membranes with nanometer size (< 2 nm) [69, 165] and sub-nm (~ 0.4 nm) defects [132] in previous experimental studies.

TMDs, on the other hand, haven't been explored experimentally as desalination membranes even though they can have a number of advantages over graphene membranes. Firstly, TMD nanoporous membranes have been predicted to have $\sim 70\%$ better permeability when compared to graphene ones, which was attributed to the presence of a combination of hydrophilic and hydrophobic atoms in the TMD de-



Figure 1.5: MD simulation of water desalination through MoS_2 nanoporous membranes, showing 70% higher permeability than graphene counterparts. Adapted from [66].

fects, giving it an effective hourglass structure, leading to better channeling of water molecules than graphene defects (Figure 1.5). [63, 66] Secondly, while ion bombardment is known to be an effective tool for fabrication of sub-nm defects in 2D materials, it alone cannot easily create defects large enough for desalination purposes in graphene due to possible defect migration [81] and carbon contamination, [119] and hence, requires specialized post-irradiation etching steps for expansion of the ion-irradiated defects. [132] However, such defect migration is expected to be fundamentally different in TMDs due to the presence of two dissimilar atoms arranged in a three-layer sandwich structure, [196] while carbon contamination is expected to be relatively less obtrusive compared to graphene (as graphene is primarily made up of carbon itself), as a result, requiring further investigation to understand the suitability of nanoporous TMD as desalination membranes. Lastly, intrinsic defects in TMD membranes are particularly susceptible to electrochemical reactivity, [6, 19, 34, 53, 111, 136] which can possibly be tuned to fabricate nanoporous membranes at low cost compared to other currently used techniques requiring high-vacuum environments. [79, 92, 109, 132, 133, 179, 188] Understanding of the underlying process is required to better explore its applicability as nanoporous membrane fabrication technique.

In Chapter 4, we develop procedures to fabricate and test nanoporous TMD membranes. We observe the effect of laser illumination on intact suspended WS_2 membranes in an aqueous environment and characterize the resulting porous membranes. We also investigate ion-irradiated MoS_2 membranes as possible selective membranes via ionic measurements through the induced sub-nm defects.

Before we move onto the experimental details of the individual projects, I will describe the fabrication steps of nanopore and nanoporous devices in the next chapter (Chapter 2), some of which are common between devices.

Chapter 2

Device Fabrication

A typical two-dimensional (2D) membrane device consists of a supporting window, or free-standing membrane, with an opening or pore in it on which the 2D membrane is suspended. Silicon nitride or silicon oxide windows are generally used as the supporting window due to the availability of well established solid state lithography techniques for silicon-based electronics. The pore in the window can be fabricated by using a focused ion beam (FIB), on which the 2D material can be transferred using either bubble transfer (for graphene), etch transfer or exfoliation. The nanopore in the 2D membrane suspended over the FIB pore can then be fabricated using a transmission electron microscope (TEM), while nanoporous membranes can be made by FIB irradiation or, in the case of TMDs, laser irradiation. This chapter describes the fabrication steps in more detail.

2.1 Support Chip Fabrication

2.1.1 Lithography

To make 2D nanopore devices, silicon-based support chips in the form of free-standing windows are first fabricated using standard solid state lithography. 4 inch diameter silicon/silicon dioxide (Si/SiO₂) wafers of thickness 525 μ m/5 μ m were ordered from NOVA Electronic Materials, LLC (<100> lattice oriented, phosphorus-doped, 1-10 Ω cm resistivity). 50 nm or 100 nm thick low stress silicon nitride (SiN_x) was deposited on both sides by Cornell Nanofabrication Facility, which serves as the support layer for subsequent 2D suspended membranes. The goal was to fabricate suspended SiN_x square windows with sides of 10-50 μ m. It should be noted here that window refers to a suspended thin membrane that is supported on all edges by the underlying thicker Si. The underlying SiO₂ plays an important role in reducing higher order device noise during ionic measurements, the thickness of which is a major factor. [8]

The entire lithography process is shown in Figure 2.1a-i. The wafer is first spincoated with negative photoresist NR7 on one side and positive photoresist S1818 on the other side. The NR7 side serves as the back side of the wafer which would be patterned using a custom negative chrome mask designed using Heidelberg DWL 66+. The chrome mask helps in patterning 5 mm x 5 mm chips with break lines at the edges and a 660 nm x 660 nm square pattern in the middle, which would serve as the backend etching window of the underlying wafer. The S1818 serves as a protective coating for the top side SiN_x layer for subsequent etching steps. The wafer is preannealed at $115^{\circ}C$ for 3 minutes, followed by patterning using Karl SUSS MA-4 or Karl SUSS MicroTec MA-6 mask aligner at 365 nm with a dose of 5 mW/cm² for 3-4 seconds and post-annealing at 115° C for 3 minutes. 7 second immersion in RD6 developer is used to remove the developed pattern. The wafer is then cleaned using DI water in an overflow bath.



Figure 2.1: (a-i) Lithography steps to fabricate free-standing silicon nitride support windows. (j) Optical image of the trench side of a wafer with ~ 100 chips. (k) SEM image of a 50 μ m x 50 μ m square free-standing SiN_x window on a SiO₂/Si substrate.

The exposed SiN_x is dry etched using Oxford PlasmaLab 80+ reactive ion etcher with SF_6 with a plasma power of 50 W and pressure of < 30 mT for 10 minutes. The underlying SiO₂ is then isotropically etched using buffered oxide etch solution (BOE, 5:1 volume ratio of 40% NH₄F in water to 49% HF in water) for 70 minutes, which also causes some under etching. It should be noted here that this under etching is taken into consideration during the chrome mask fabrication, to make sure the final SiN_x window has the desired dimensions. To verify that all of the SiO₂ is etched away, Filmetrics F40 film thickness meter is used to measure SiO₂ thickness at multiple patterned locations.

The residual photoresist is stripped off using acetone/isopropanol before the wafer is immersed into a 40% by weight KOH solution. The solution is heated to 70C and stirred using a magnetic stirrer. The KOH etches the exposed Si anisotropically at an angle of 54.7° to the <100> top side to form tetrahedral pits which end into square windows of SiO₂/SiN_x on the other side of the wafer. The process is run for ~ 22 hours till the Si pits are terminated by the SiO₂. This is verified by checking for the square windows in an optical microscope every 30 minutes after the first 20 hours of etching. The variability in the etching times give rise to a range of window sizes between 10-50 μ m. Finally, DI water is used to clean the wafer.

S1818 is drop coated on the SiN_x side to protect it from the next etching step, and left to dry overnight in a fume hood. The wafer is then immersed in the BOE for 110 minutes, making sure there are no air bubbles trapped in the Si pits, to etch the underlying SiO₂ and release the SiN_x windows, which bulge up to form the final windows. Finally, the resist is removed using acetone/isopropanol. A finished wafer containing ~ 100 chips and a scanning electron microscope (SEM) image of an ideal 50 μ m SiN_x window are shown in Figure 2.1j and k, respectively.

2.1.2 Focused Ion Beam (FIB)

Focused ion beam (FIB) is an instrument which scans a focused beam of ions, like gallium (Ga⁺) or helium (He), over a sample and, by measuring the amount of ions scattered, can construct an nanoscopic image of the sample. Due to the higher kinetic energy of the ions compared to electrons (which is used in a similar fashion in a scanning electron microscope or SEM to image samples), FIB can also be used to ablate, deposit and pattern materials. For our purposes, we use a FIB to drill pores in our free-standing windows by focusing the ion beam on single spots instead of scanning it.

To suspend the 2D material, a pore is drilled near the center of the SiN_x window using Ga⁺ focused ion beam (FIB) FEI Strata DB235 instrument, shown in Figure 2.2a-b. An acceleration voltage of 30 kV and an ion beam current of 1-10 pA is used in the spot mode to obtain a circular (if the ion beam is well aligned) or elliptical (if the ion beam has astigmatism) pore with an effective diameter of 60-200 nm in a 100 nm thick SiN_x window. The beam was calibrated and it was observed that the minimum pore size (effective diameter ~ 60 nm) was obtained for 1 pA ion beam current and a spot mode drilling time of ≥ 4 seconds for a perfectly aligned ion beam. A shorter time would thin the window without actually drilling through (Figure 2.2f). Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of various sized FIB pores obtained from different doses are shown in Figure 2.2c-d and e, respectively.

The size of the suspended 2D material area, *i.e.*, the FIB diameter, plays a role in the noise of the device during ionic measurement, strength of the 2D membrane and



Figure 2.2: (a) A FEI DB235 FIB instrument showing the FIB column, SEM column and sample chamber. (b) As the FIB column and SEM column are aligned at an angle of 54° to each other, the sample window is located using the SEM and then rotated before the FIB drilling is performed. (c-d) SEM images of FIB drilled regions for various ion beam currents and drilling times. SEM images are not enough to determine whether the pore has formed due to its resolution limit. (e) TEM image of the smallest FIB hole that can be drilled (effective diameter ~ 60 nm) using the FEI DB235 FIB instrument. (f) TEM image of a typical FIB thinned region obtained for drilling times < 4 s at 1 pA ion beam current.

can also affect the ionic conductance of the pore (if the FIB diameter is comparable to the actual 2D nanopore diameter). As a result, care should be taken when making the FIB pores depending on the requirements of the device application.

Suspending 2D materials on large FIB pores can lead to tears and weak membranes, or partial coverage. As a result, for applications requiring a large 2D suspended area, like desalination, array of FIB pores can be used to make multiple smaller 2D membranes which is more resilient than a single large membrane. This



Figure 2.3: (a) SEM image of the smallest FIB pore of 400 nm achieved in patterning mode with ion beam current of 100 pA and dwell time of 0.8 s. (b-c) SEM images of the FIB array with individual pore diameters of 400 nm and inter-pore distance of 5 μ m.

can be achieved by designing and loading a patterning mask for the FIB software and running the FIB ion beam scan. As the patterning happens in scanning mode, the drilling times are different when compared to spot mode, thus requiring fresh calibration. It was found that for small beam currents (1-10 pA), very high beam dwell times, *i.e.*, time the beam spends at each spot of the pattern, are generally required leading to either unfeasible total patterning time or drifting of beam during patterning. After calibration, a beam current of 100 pA and beam dwell time of 0.8 s was found to give FIB pores with ~ 400 nm diameter reproducibly. A typical FIB array fabricated using the above parameters is shown in Figure 2.3.

2.2 Graphene

2.2.1 Growth

Chemical vapor deposition (CVD) was used to grow graphene using copper as a catalyst. 99.999% pure copper foil (Alfa Aesar) was cut into rectangular sheets and cleaned using a 30% by volume HCl solution. The foil was then put on a quartz boat, inserted in a 1-inch-diameter tube furnace and heated up to 1050°C in argon (Ar) and hydrogen (H₂) at flow rates 350 sccm and 20 sccm, respectively, at a ramp rate of ~ 50°C/min. It was followed by annealing at 1050°C in 500 sccm Ar and 20 sccm H₂ for 15 minutes, followed by cooling to the growth temperate of 1000°C at a ramp rate of -10°C/min. 500 sccm Ar, 20 sccm H₂ and 10 sccm methane (CH₄) were flowed through the tube for 15 minutes at 1000°C followed by turning off CH₄ and rapid cooling to facilitate graphene nucleation and growth on top of the copper catalyst. This growth was used to obtain film of monolayer graphene. The growth schematic is shown in Figure 2.4.



Figure 2.4: CVD growth of graphene.

2.2.2 Characterization

The graphene obtained using the previously described growth method is generally large continuous monolayers. To confirm the monolayer character and the quality of the graphene, Raman spectra was obtained at multiple positions on the graphene. The acquisition was done on a Raman NT-MDT Nova upright Raman system using a 532 nm laser as the excitation source with filtering such that the sample was exposed to < 3 mW laser power to avoid sample heating and/or deterioration.



Figure 2.5: Raman spectra of monolayer graphene.

The background noise from the copper substrate was fitted by a polynomial function and subtracted. The remaining two distinct peaks at 1578 cm⁻¹ (G peak) and 2685 cm⁻¹ (2D peak) were fitted to single Lorentzians. The presence of a single, narrow Lorenztian shape of the 2D peak, with a small full-width-half-maximum or FWHM ($\sim 28 \text{ cm}^{-1}$) generally confirms monolayer characteristics, while the presence
or absence of the defect peak, normally appearing at 1350 cm^{-1} , gives an indication of the quality of the graphene. Raman spectra obtained from our monolayer graphene is shown in Figure 2.5.

2.2.3 Bubble Transfer

The use of a conducting growth catalyst (copper) allows the possibility of using an ionic solution and voltage bias to delaminate the graphene from its copper growth substrate without affecting the graphene.

The graphene-on-copper foil was cut into 5 mm x 5 mm individual pieces (same as the chip dimensions), each of which was taped to cover slips by the edges. Each of the cover slips were spin-coated with PMMA at 4000 rpm for 45 seconds, followed by drying at room temperature (RT) for at least 5 minutes. The foil piece was carefully untaped from the cover slip, ensuring minimum number of creases on the foil, and straightened by pressing it between two cover slips lightly. A springy tweezer was used to hold the foil by the edges, which were not coated with PMMA, and was slowly immersed in a 1.2 M sodium hydroxide (NaOH) solution. An 8 V voltage was applied between the copper/tweezer (-ve) and a graphite electrode (+ve) dipped in the NaOH solution using a voltage source. This voltage bias results in formation of H₂ bubbles due to electrolysis of water at the copper-graphene interface, [37, 54] thereby delaminating the PMMA-graphene layer off the foil. The transparent PMMAgraphene layer was then scooped off from the NaOH solution with the help of a small piece of hydrophobic polyethylene terepthelate (PET) and transferred to DI water. This was repeated multiple times to remove the bubbles stuck underneath the graphene and also to remove any salt contamination from the NaOH solution. The major steps of this process is illustrated in Figure 2.6.



Figure 2.6: Bubble transfer of graphene.

Prior to transfer, the silicon nitride chip was cleaned using Piranha solution (1:3 by volume $H_2O_2:H_2SO_4$) at 200°C for at least 20 minutes. This not only cleans the chip from organic impurities but also makes it hydrophilic, which makes it easier to scoop the PMMA-graphene layer from the water. After scooping the PMMA-graphene layer onto the chip, the chip was allowed to dry overnight in the fume hood at RT. The PMMA was then removed by immersing the chip in acetone for at least 30 minutes and subsequently cleaning it with isopropyl alcohol (IPA). The chip was dried with a nitrogen gun and annealed in a rapid thermal annealer (RTA) at 350°C

for 90 minutes in 95% Ar/5% H₂ environment.

2.3 Tungsten Disulfide (WS $_2$)

2.3.1 Growth

 WS_2 monolayers were synthesized by CVD through a method reported by Kim *et* al. [75] First, a rectangular piece of silicon oxide (SiO_2) substrate was cleaned using Piranha solution and UV ozone. It was then spin-coated with solutions of 2% sodium cholate and ammonia metatungstate (15 mM) at 4000 rpm for 15 seconds each. After the substrate dried, it was positioned in the middle of a 1-inch-diameter one-zone tube furnace in addition to \sim 70-100 mg sulfur powder on a small silicon piece, which was placed upstream at a certain position from the middle of the furnace such that the sulfur temperature reached 150° C when the actual furnace temperature reached 800°C (the growth temperature). This temperature-position calibration was done beforehand using a thermometer. After the tube was flushed with 1000 sccm Ar for 20 minutes, the furnace was heated up to 800° C with 100 sccm Ar at a ramp rate of \sim 70°C/min and H_2 was introduced at a flow rate of 15 sccm. After 10 minutes, the H_2 was turned off and the substrate was rapidly cooled to RT by pushing the tube out of the furnace and turning the furnace off. Although this growth method gives a range of flake densities, the percentage and size of the monolayer flakes are good enough for our purposes. The growth schematic is shown in Figure 2.7.



Figure 2.7: CVD growth of WS_2 .

2.3.2 Characterization

WS₂ grown by the above methods produces triangular flakes ranging between monolayer and few-layers with a majority population of monolayers, and flake side length of 10-50 μ m. Monolayers of WS₂ can be easily distinguished by their almost transparent appearance (compared to more opaque few-layer flakes) on the growth substrate in an optical microscope. Figure 2.8 shows the material characterization of vapor-grown WS₂ triangular monolayers.

Atomic force microscope (AFM) scans were performed in a Bruker Dimension Icon operating in tapping mode. A uniform thickness of ~ 0.7 nm is the ideal thickness for a monolayer flake. [164]

Raman spectroscopy was performed in a NT-MDT NTEGRA Spectra with an excitation laser wavelength of 532 nm with spectral resolutions of 0.5 cm⁻¹. The Raman spectrum of monolayer WS₂ consists of the four primary modes - first-order in-plane acoustic mode, LA(M) (175 cm⁻¹), second-order in-plane acoustic mode,



Figure 2.8: (a) AFM scan of a monolayer WS₂ flake. The line profile in white indicates a thickness of 0.7 nm, which corresponds to a monolayer. (b) Raman spectra ($\lambda = 532$ nm) of a monolayer WS₂ flake with indicated primary modes. (c) Photoluminescence (PL) spectra of a pristine suspended monolayer WS₂ membrane showing three spectral components: neutral exciton (X₀), trion (X_T), and defect (X_D). (d) Gaussian blurfiltered AC-HRSTEM lattice image taken at 80 kV. The inset is a SAED pattern with expected (100) and (110) diffraction spots. Adapted from references [34] and [33].

2LA(M) (353 cm⁻¹), first-order in-plane optical mode, E' (Γ) (357 cm⁻¹), and firstorder out-of-plane optical mode, A₁' (419 cm⁻¹) - and their derivative peaks. [164] The higher relative intensity of the 2LA(M) to A₁' mode and the absence of a peak at ~ 310 cm⁻¹ can suggest high monolayer quality of a flake. [205]

Photoluminescence (PL) measurement can also be used to confirm whether the flake is monolayer. An excitation wavelength of 532 nm (spot size = 940 nm) and incident laser power of ~ 50 μ W were used to prevent unwanted laser-induced degradation during measurements. [19] A very strong PL signal obtained near the direct bandgap value of WS2 (~ 2.05 eV) can verify the monolayer quality of a flake. [64] The spectrum is curve-fitted to three Lorentzian components - namely the neutral exciton (X₀), the trion (X_T) and the defect-related (X_D) peaks, which are centered around ~ 2.02, 1.99 and 1.88 eV, respectively. [24, 34] The average spectral weight percentages of the X₀, X_T and X_D peaks for our monolayer as-grown flake was observed to be ~ 74%, 25% and 1%, respectively.

Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns taken in a JEOL JEM-2010F TEM operating at an accelerating voltage of 200 kV provides information about the lattice orientation and quality of the suspended regions. However, devices on which ionic measurements are performed are not subjected to such high electron accelerating voltages, as 2D materials can get easily damaged by the high energy electron beam. High-angle annular dark field (HAADF) aberration corrected high resolution scanning transmission electron microscope (AC-HRSTEM) images obtained in FEI Titan G2 S/TEM operating at an accelerating voltage of 80 kV causes less damage and was used to obtain atomic resolution images of the suspended membranes. A Gaussian blur filter was applied to the AC-HRSTEM images using ImageJ software in order to reduce contrast from carbon contamination.

2.3.3 KOH-Etch Transfer

The WS₂-SiO₂ growth substrate was broken into ~ 5 mm x 5mm or ~ 10 mm x 5 mm pieces using a diamond cutter, and spin coated with PMMA at 4000 rpm for 45 seconds. The pieces were allowed to dry in the fume hood at RT for at least 5 minutes and then carefully dropped on the surface of 1M KOH solution being heated at 75°C. For the 10 mm x 5 mm pieces, the PMMA coated substrate was first scratched through the middle using a razor before putting it in KOH. This was done so that the PMMA-WS₂ layer separates into 5 mm x 5 mm chip-sized sections during the etch. Once the underlying SiO₂ etches away, the substrate sinks into the solution leaving

the PMMA-WS₂ layer afloat, which was transferred to DI water using a PET sheet to clear off any bubbles and clean salt contamination. After being washed in DI water for at least 1 hour, the flakes were then transferred using one of two methods described next. For both the methods, the SiN_x chip was subjected to Piranha cleaning before the transfer.

Micropositioning

The first method is a micropositioning technique which is useful for growth with low flake density and is illustrated in Figure 2.9. The $PMMA-WS_2$ layer was scooped from the DI water bath using a glass slide with the WS_2 side down and allowed to float on top of the glass slide. A glass slide with double-sided Kapton tape was pressed over the PMMA to secure it to the tape being careful that no folds appeared on the PMMA. The glass slide with the PMMA was aligned over the SiN_x window, which was secured to a separate glass slide, with a micromanipulator attached to an optical microscope. Two Kapton tape pillars were attached to the substrate slide edges to help achieve good contact between the flake slide and the substrate slide. A monolayer flake was selected on the PMMA in the optical microscope and the micromanipulator was used to position the flake over the SiN_x window. The flake was lowered onto the sample until it contacted with the substrate and pressure was applied to secure the two slides together. The final SiN_x assembly was detached from the micromanipulator and immersed in an acetone bath overnight. The substrate separates from the assembly in acetone and was cleaned with ispropanol and dried with N₂ before annealing at 300°C for 90 minutes in 95% Ar/5% H₂. Annealing was a crucial step as it was found to prevent delamination of the flakes when the device interacts in a liquid environment during ionic measurements.



Figure 2.9: (a-f) Major steps of the micropositioning procedure. (g) The desired flake (red) during alignment is visible under the optical microscope through the glass, tape, and PMMA and is positioned over the SiN_x window. (h) The flake after being lowered onto the sample showing good contact between the flake and the final substrate surface, as evidenced by the substrate surface and flake being in the same focal plane. (i) SiN_x window with the transferred flake post overnight acetone bath. All scale bars are 40 μ m. Adapted from [124].

The flake quality was studied after transfer to verify that the transfer method did not dramatically degrade the material. The flake was transferred from the original 300 nm SiO₂/Si wafer growth substrate to a 150 nm SiO₂/Si wafer substrate. In order to check the quality of the transferred WS₂, the flake was characterized optically, with atomic force microscopy (AFM), and using Raman spectroscopy before transfer, after transfer, and post thermal annealing. The results of the flake characterization is shown in Figure 2.10.



Figure 2.10: (a) Optical image of flake, pre-transfer, on growth substrate. (b) AFM image of flake in (a) before transfer. (c) Raman spectrum of flake in (a) showing the characteristic WS_2 peaks at 351, 356, and 417 cm⁻¹. (d) Optical image of flake post transfer, on the silicon oxide substrate. (e) AFM of flake in (d). (f) Raman spectrum of the transferred flake in (d) showing the same characteristics peaks as in (c). Adapted from [124].

Optically, there was no change observed in the flake throughout the transfer process. Inspection of the flakes by AFM indicated that some creases form in the flake post transfer and that the edges get damaged by the KOH etching, but the flake remained otherwise intact. From the AFM scan, it was also observed that the annealing step decreases the leftover PMMA on the surface. The changes in the Raman spectra of the flakes before, after transfer, and post annealing show the existence of in-plane strain from the growth process, the release of this strain after transfer, and the conforming of the flakes to their new substrate after the annealing process.

Detailed results, including effect of substrate and annealing on transferred flakes,

of this micropositioning technique has been published in the article "Transfer of Monolayer TMD WS₂ and Raman Study of Substrate Effects" by Mlack, J.T., Das, P.M., Danda, G., Chou, Y.C., Naylor, C.H., Lin, Z., López, N.P., Zhang, T., Terrones, M., Johnson, A.C. and Drndić, M., Scientific Reports, 7, pp. 43037 (2017).

Wet Transfer

The second method is used for growths with high flake density. In this method, the PMMA-WS₂ layer is scooped out of the DI water using the SiN_x chip and is checked for any flakes on the window in the optical microscope. If no flakes get positioned on the window, the flake is floated back in the DI water and the process is repeated. For most of our chips and high density growth we grew, it took a maximum of 15 attempts (~ 20 minutes) to get a flake on the top of our windows. The chip is finally cleaned in acetone for at least 24 hours, followed by isopropanol and RTA. This method is facile, quicker and cleaner compared to the micropositioning method, but it requires a higher flake density which is not consistently achievable. Optical images of some of the successful transfers are shown in Figure 2.11.



Figure 2.11: Transferred WS_2 flakes on windows with FIB holes.

2.4 Nanopore Fabrication

2.4.1 Transmission Electron Microscope (TEM) Drilling

Fabricating solid-state nanopores using focused electron beam has been around for almost 15 years. [40, 163] In this process the thin suspended membrane is loaded into a transmission electron microscope (TEM) and the electron beam is focused to ablate atoms to form nanopores. While SiN_x nanopores can be fabricated quite easily using this method, 2D materials face a number of challenges due to its intrinsic atomic thinness - (i) damage at high electron accelerating voltages common in TEM even during viewing of the sample, and (ii) carbon contamination during electron beam scanning. But recent advances in the nanopore fabrication process have been able to overcome these problems reasonably well.



Figure 2.12: (a) JEOL JEM-2010F TEM setup and TEM image of a 10-nm-diameter pore (outlined in red) drilled with it in the STEM mode. (b) FEI Titan G2 S/TEM setup and AC-STEM image of a pore with an effective diameter of ~ 1.1 nm drilled with it in the STEM mode. Adapted from [168].

It has been previously demonstrated that the TEM can be used in the scanning mode (STEM mode) to reduce the damage of 2D materials while viewing the sample even at high accelerating voltages. [144] Using this technique, nanopores were drilled in our suspended 2D membranes using a 200 kV JEOL JEM-2010F TEM operating in STEM mode with a spot size of 1 nm, drilling time of 3-5 s and an electron beam dose of $\sim 10^4 \text{ e}^{-}/\text{nm}^2$. Nanopore diameters of 3-10 nm were achieved consistently using this method (Figure 2.12a).

Lower electron beam damage of the membrane and smaller nanopores with atomic precision (diameters < 2 nm) can be obtained by using high resolution aberration corrected scanning TEM (AC-STEM) operated at low accelerating voltages (Figure 2.12b). For our experiments, we used FEI Titan G2 S/TEM operated at 80 kV. [168]

To reduce carbon contamination in our membranes, the chips were subjected to RTA at 300°C for 90 mins before TEM processing. After putting the sample inside the TEM, the electron beam was allowed to scan near the suspended membrane on the thick SiN_x support region to facilitate deposition of any carbon contamination away from the membrane before the actual drilling was performed.

2.5 Nanoporous Membrane Fabrication

2.5.1 FIB Irradiation

Ion-induced damage of suspended 2D membranes can be used to fabricate nanoporous membranes with sub-nm defects. [18, 122, 168] Suspended 2D flakes were irradiated with Ga⁺ ions using the ion gun of a FEI Helios dual beam instrument. To perform the Ga⁺ ion irradiation, the acceleration voltage was set to 30 kV and the current intensity to 230 pA. The beam incidence was normal to the surface and followed a raster path over a rectangular area, 410 μ m long and 274 μ m wide. The beam

impinges the sample in imaging mode, in this condition the beam dwelled 50 ns in each step; the spacing between steps was approximately 260 nm. Finally, the different doses on the single-layer 2D flakes were achieved by manually varying the irradiation time. The population distribution of defects and the properties of such nanoporous membranes thus formed are further elaborated upon later in Section 4.3.



Figure 2.13: (a) FIB irradiation schematic and (b) AC-STEM image of the corresponding nanoporous membrane for a FIB irradiation does of 2.50×10^3 ions/cm² with zoomed-in images of individual defects. Adapted from [168].

2.5.2 Laser Irradiation

TMDs are known to undergo photo-oxidation, accelerated by the use of lasers and highly oxidizing environments. [6, 19, 34, 111, 136] While studies have been performed on how to prevent this damage by encapsulation, [2] these photo-induced damage, if controlled, can be useful in the fabrication of nanoporous TMD membranes.

A custom setup was built to enable laser irradiation of suspended TMD membranes as shown in Figure 2.14. Suspended membranes were immersed in deionized (DI) water and located optically using a 60X water immersion objective lens and an



Figure 2.14: Laser irradiation setup.

integrated CMOS camera. A green laser ($\lambda = 532$ nm, P = 5 mW) was then focused on selected membranes for a specific irradiation time with different laser power densities or irradiation doses modulated using a step variable neutral density (ND) filter (Thorlabs). DI water serves a dual purpose in reducing the spot size of the incident laser (540 nm) by allowing for a higher numerical aperture (NA) objective lens, while also providing the necessary oxidizing environment for the photo-oxidation reaction. [2, 6, 136] All cables were kept electrically isolated or grounded to reduce any cross-talk. Alignment was performed by first focusing the laser on a white piece of paper and observing it using the CMOS camera. The laser spot was then centered and digitally marked in the image capture software window by changing the mirror orientations. This spot was then aligned to the nanopore device windows mounted on the micromanipulator stage with the laser beam turned off.

Besides the ND filter, another power control that was available was the laser driving current, which, in our case, could be varied from 0.18 mA to 0.28 mA without harming the laser. Calibration of the laser irradiation dose was performed by varying both these values (*i.e.*, ND value and laser driving current), as shown in Figure 2.15.



Figure 2.15: Laser power density calibration.

It should be noted that use of the dichroic mirror in the setup is required for image capture by the camera and reduces the laser power reaching the sample. As a result, laser irradiation dose calculations were performed using power values measured at the sample stage using a power meter. In our experiments, the laser irradiation dose was varied between $\sim 10^2$ and 10^5 W/cm², which is lower than the dose required for laser-induced thermal ablation of TMDs (MoS₂). [19] Further analysis of the defects and their dependence on the laser power density is explained in Section 3.3.

2.6 Experimental Setup

2.6.1 Ionic Measurements

Ionic measurements of nanopore membranes are performed by enhancing the ionic current signal through the nanopore with a low-noise, current amplifier. Due to the hydrophobicity and low chemical resistance of 2D materials, the devices need to be made hydrophilic using chemically softer pre-measurement treatments than Piranha, which is most commonly used for silicon-based nanopore devices.

The 2D nanopore or nanoporous devices were mounted on a PDMS platform using Kwikcast sealant over an underlying channel for ionic fluid, and were placed in a beaker containing ethanol:water (v/v 1:1) solution for at least 30 minutes. Bubbles were removed using a pipette every 10-minute interval. The platform was removed and the solution was carefully replaced with water, followed by the desired ionic solution in the channel underneath (trans reservoir) and a drop on the top (cis reservoir). Ag/AgCl electrodes were used to perform ionic measurements with EPC-10 HEKA (sample rate = 50 kHz) amplifier. 1 M KCl (with 10 mM EDTA and 1 mM Tris; measured solution conductivity = 11.8 S/m, pH = 8.7) and 3 M KCl (with 30 mM EDTA and 3 mM Tris; measured solution conductivity = 30.2 S/m, pH = 7.8) solutions were prepared using DI water and the conductivity and pH were measured with Accumet XL-20 pH conductivity meter. DNA translocation data obtained from single nanopore devices was analyzed using Pypore (https://github.com/parkin/pypore) and custom Python scripts.

Chapter 3

2D Nanopore Devices

3.1 Introduction

Two-dimensional nanopore sensors are promising for a range of applications, as well as testbeds for probing the physics of low-dimensional systems. Number of challenges still exist in commercialization of such sensors due to the use of traditional lowyield nanopore fabrication method involving TEM electron beams. In addition, high DNA translocation speeds through such nanopores results in low temporal resolution making it difficult to achieve DNA sequencing - one of the main applications of nanopore sensors.

Graphene nanopores were the first 2D material demonstrated to be able to detect DNA translocation with very high sensitivity. [121, 152] However, the DNA translocation speed was found to be ~ $20-100 \times 10^6$ nucleotides/s, requiring a much higher detection bandwidth (> 10 MHz) for single-base resolution than that of commercially

available signal recorders (bandwidth < 1 MHz). Attempts have been made on trying to slow down DNA translocation by applying a voltage to the graphene nanopores, sandwiched between insulating layers of aluminium oxide [174] but the use of thick oxide layers (~ 20 nm) defeats the purpose of using atomically-thin 2D nanopores. For thinner insulating membranes, leakage current from the graphene membrane becomes an important factor to consider. In the second section of this chapter, we fabricate graphene nanopores, insulated on both side with 3 nm TiO₂, and measure the leakage current for various electrical configurations. We determine a voltage range for which the graphene and potassium chloride electrolyte seem to interact the leakage current can be further reduced by shrinking the area of graphene exposure to the ionic solution, and predict that the gating control can be enhanced by reducing the molarity of the electrolyte.

Tungsten disulfide (WS₂) monolayers exhibit a direct bandgap and strong photoluminescence (PL) in the visible range, [11, 137, 199] and is known to undergo laser-induced electrochemical reactions in an oxidizing environment giving rise to defects. [2, 53] Understanding the mechanism behind the formation of such defects can provide us with the tools to help fabricate and dynamically control them using optical excitation for a nanopore oriented scenario. In the first section of this chapter, we fabricate nanopore devices based on WS₂ and determine their suitability in detecting DNA translocations. We also investigate the effect of laser illumination on the nanopore size and find that the nanopore size expands in solution, the rate of which is controllable by modulating the laser power density.

3.2 Voltage-Controlled Graphene Nanopores

3.2.1 Background

Monitoring field-driven ionic flow through nanopores is one approach proposed to realize ultrafast DNA sequencing. [16, 120, 129, 151, 173] A nanopore device separates two chambers containing electrolyte solution and voltage is typically applied across the nanopore to drive ions and DNA molecules through the nanopore while recording ionic current. Nanopore-based sequencing could be achieved by measuring the distinct current reductions from individual DNA bases, [47, 175] as demonstrated by using solid-state nanopores. Among solid-state nanopores, nanopores in two-dimensional (2D) materials such as graphene, [121, 152] transition metal dichalcogenides (TMDs) [34, 103] and boron nitride [209] have attracted attention recently because of their potential to realize single-base resolution.

In addition to requiring thin nanopores for DNA sequencing, high bandwidth electronics (> 10 MHz) [148, 155] is also needed because of high DNA translocation velocities in typical measurements, which is \sim 1 Mbases/s for silicon nitride membranes [175] and \sim 25-100 Mbases/s for 2D membranes. [34, 56, 103, 121, 152, 209] In the absence of such electronics, a possible approach is to decrease translocation speed, although this also decreases the sequencing speed. Numerous efforts to slow down DNA translocation have been explored over the last decade using biological enzymes, [22], nanoparticles, [73] different electrolytes, [38, 47, 83, 201] temperature, [12, 51, 193] pressure [200] and by manipulating interactions between DNA and nanopore/membrane. [10, 84, 88] Controlling the voltage profile inside of a nanopore is another idea put forth towards achieving control over translocation speed by electrically gating the flow of ions [61, 127] and DNA molecules. [3, 65, 108] In the case of 2D membranes, realizing such proposals may be feasible with graphene nanopores [204] because of the excellent electrical conductivity of graphene, in addition to its single-atom thickness. While most of the predictions of slowing down DNA via voltage gating are from a theoretical standpoint, [3, 65, 108] limited experimental investigation exist regarding this aspect till now. [174] This is because leakage current between the graphene and the ionic solution comes into play in such a system and can lead to high noise in the system. [9]

To explore the feasibility of controlling the voltage profile inside graphene nanopores, in this section, we study the ionic current characteristics of graphene nanopore devices when voltage is applied to graphene, investigating the electrochemical leakage effects. We obtain leakage current curves for intact graphene membranes in KCl solution and extract a voltage range in which leakage is minimal. We next investigate the effects of voltage sweep rate, thin oxide insulation (3 nm TiO₂) and the area of membrane exposed to the ionic current on the leakage current. TiO₂ coated graphene nanopores were fabricated and gating of ionic current through the nanopore was performed by applying a graphene voltage such that the relative voltage bias between the graphene and the electrodes remained within the previously determined low leakage range.



Figure 3.1: (a) Raman spectra of CVD graphene grown on copper, with copper background subtracted. Device schematic of suspended intact (a) bare and (b) TiO_2 coated graphene membranes.

3.2.2 Device Fabrication

Graphene was grown on a copper (Cu) substrate by chemical vapor deposition (CVD) developed previously [121] and characterized using Raman spectroscopy (Figure 3.1a). To verify the monolayer character and the good quality of our graphene layers, Raman spectra was obtained at multiple positions on the grown graphene. Acquisition was done with a Raman NT-MDT Nova upright Raman system using a $\lambda = 532$ nm laser as the excitation source with filtering such that the sample is exposed to < 3 mW of power to avoid sample heating and/or deterioration. The background noise from the copper substrate was fitted by a polynomial function and subtracted. The remaining two distinct peaks at 1578 cm⁻¹ (graphene G peak) and 2685 cm⁻¹ (2D peak) were best fitted with single Lorentzians. The single Lorenztian shape of the 2D peak, with a full width at half maximum (FWHM) of 28 cm⁻¹ confirms the single layer characteristic of our sample. The absence of the defect peak, normally appearing at 1350 cm⁻¹, confirms the good quality of our graphene monolayer. [62]

50-nm-thick suspended SiN_x windows on 5 μ m SiO₂/500 μ m Si wafer was fabricated using photolithography. [34, 121] A ~ 600 nm diameter hole (area ~ 0.3 μ m²) was drilled in the membrane using a focused ion beam (FIB) instrument (FEI Strata DB235) with a 30 kV Ga⁺ source (Figure 3.1b(inset)). The graphene was transferred onto the membrane using bubble transfer [37, 54] followed by rapid thermal annealing (RTA) at 350°C for 1.5 hours (Figure 3.1b). Silver paste was then used to paint electrical connection pads on two far sides of the graphene layer.

Two different types of nanopore samples were investigated for leakage measurements. One contained bare suspended graphene and the other contained suspended graphene coated with thin, 3-nm-thick TiO_2 layers, thermally evaporated on both sides of the membrane, as shown in Figure 3.1b and c, respectively.

TiO₂ was previously shown to be a good protective coating for graphene membranes that becomes hydrophilic after exposure to UV-ozone, making the formation of ionic channels (*i.e.*, wetting) through hydrophobic graphene nanopores much easier. [121] The thickness of TiO₂ is kept small so that the total thickness of nanopores is limited to 7 nm or less, to achieve high ionic current signals required for DNA detection [34, 47, 56, 103, 121, 152, 209] while also protecting the underlying graphene during the UV-ozone treatment.

In the case of TiO₂ covered graphene, the thickness of the TiO₂ coating (~ 3 nm) is too small to uniformly cover the macroscopic roughness of the silver pads on the graphene and prevent electrical connection. Proper connection between the silver electrodes and the graphene was verified by applying voltage across the two silver pads using Keithley 2400 SourceMeter and calculating the graphene sheet resistance between the silver electrodes. The sheet resistance value was obtained to be in range of 2-11 kΩ/sq, which matches well with literature values for sheet resistance of monolayer undoped graphene. [9, 15, 59, 130, 202]

It should be noted that we refer to the two sides of chips as the top and bottom sides, where the bottom side refers to the trench face of the device.

Current measurements were performed using HEKA EPC 10 USB Triple patch clamp amplifier with signal filtering at 10 kHz. Voltage sweeps for leakage measurements were performed by maintaining the voltage at a constant value for a specific time interval before ramping up to the next voltage step. We define the sweep rate (dV/dt) to be the ratio of the unit step voltage to the unit step time. Thus dV/dt= 100mV/10s would mean the current was measured at 100mV intervals with each voltage level held constant for 10s. All measurements were performed in 1M KCl, 10mM Tris, 1mM EDTA solution (pH = 9.5, $\sigma = 11.11$ S/m).

3.2.3 Leakage Current in Intact Membranes

Figure 3.2 shows the experimental setup and the current schematic to measure the leakage current between the top electrode and the top side of the device (I_{TG}) as a



Figure 3.2: Measurement setup schematic for leakage measurement between the electrode and top side of intact membranes. Only TiO_2 covered device is shown here, but bare graphene devices were also measured using the same setup.

function of graphene voltage relative to the top electrode or top-to-graphene voltage (V_{TG}) . I_{TG} vs. V_{TG} was measured for bare graphene devices and TiO₂-covered graphene devices with intact membranes in 1M KCl solution to study the dependence of the I_{TG} on V_{TG} sweep rate, and the presence of TiO₂ coating.

Figure 3.3a shows the I_{TG} - V_{TG} characteristics of a TiO₂ covered graphene membrane measured at a voltage sweep rate (dV/dt) of 5 mV/s. We observe a nonlinear trend showing high leakage currents of > 6 nA for V_{TG} < -0.2 V and V_{TG} > +0.6 V (high leakage region). For -0.2 V < V_{TG} < +0.6 V (low leakage range), I_{TG} is almost constant with change in V_{TG} and average $|I_{TG}|$ < 6 nA. This diode like behavior suggests that some form of charge transfer must be happening between the graphene and the electrolyte. As the threshold graphene voltage for large leakage current is negative (~ -0.2 V), charge transfer should be happening with relative ease between graphene and potassium (K⁺) ions [110, 141] than between graphene and chloride (Cl⁻) ions, which are the corresponding ion species dominating the electric double



Figure 3.3: (a) Leakage current-voltage measurement of a TiO₂ coated intact graphene membrane showing a non-linear curve with a current peak at ~ 0 V during the forward sweep. (b) Current trace during the current peak when the graphene voltage is switched from -0.1 V to +0.1 V.

layer (EDL) at the graphene-electrolyte interface for negative and positive graphene voltages, respectively.

Hysteresis was observed in the measured leakage current for the whole voltage range with a leakage current peak at ~ 0 V only in the forward sweep (I_{peak}). I_{peak} was consistently seen for all devices, though the magnitude varied from sample to sample. The peak only appeared when graphene voltage switched from negative to positive with respect to the Ag/AgCl electrode.

To investigate the origin of I_{peak} , V_{TG} was switched from -0.1V to +0.1V and kept constant at +0.1 V, and the corresponding I_{TG} trace was obtained as a function of time (Figure 3.3b). The leakage current was seen to decay exponentially with time, resembling discharging of an RC circuit. This suggests that the observed I_{peak} might be related to discharging and charging of the EDL at the graphene-electrolyte interface. The origin of the I_{peak} might be from the accumulation and strong binding of K^+ ions to the graphene at negative graphene voltage (leading to continued charge transfer), [110, 141] thereby making it harder for Cl^- to replace them when the voltage is switched.



Figure 3.4: (a) Leakage current dependence on voltage sweep rate showing higher leakage currents at slower sweep rate. (b) Leakage current comparison between bare and 3 nm TiO_2 coated intact graphene membranes, showing similar leakage currents.

To study the dependence of the leakage current on the voltage sweep rate, we measured I_{TG} for different sweep rate of the same device, as shown in Figure 3.4a. It was seen that the I_{TG} value decreased in the high leakage regions for faster sweep rate (*i.e.*, lesser time at each voltage). Such a trend is possible if the interaction between the electrolyte and graphene is reduced at a faster sweep rate. K⁺ ions cannot accumulate fast enough at the interface at faster sweep rate due to the finite speed of ions, which can give rise to smaller leakage currents. This suggests that the concentration of ions at the graphene-electrolyte interface also plays an important role in the leakage current.

It should be noted that this experiment was repeated for different devices at same

sweep rates and the average I_{TG} at $V_{TG} = -0.5$ V was seen to vary considerably. This can be attributed to the variation in the number of defects (or active sites) exposed to the electrolyte for different devices. The overall leakage trend and low leakage region range (-0.2 V < V_{TG} < +0.6 V), however, remained the same.

Since graphene is hydrophobic, graphene nanopores need to be processed to allow formation of an ionic channel through the nanopore (or wet the pore). As seen previously, [121] although UV ozone helps wetting of the nanopore, it damages the graphene membrane and results in graphene having more reactive sites, which can increase leakage current. In order to protect graphene from UV damage, we coat the graphene layer with 3 nm TiO₂ layer. This provides us a medium to wet the nanopore in nanopore devices while also protecting the graphene from UV ozone. To check the efficiency of the 3 nm coating, the sheet resistance of graphene (R_s) was measured before and after 15 minutes UV-ozone treatment and was found to be similar (before UV: $R_s \sim 12 \text{ k}\Omega/\text{sq}$ & after UV: $R_s \sim 9 \text{ k}\Omega/\text{sq}$).

The leakage characteristics for bare and 3 nm TiO₂ covered intact graphene membranes was compared for the same sweep rate (50 mV/s) as shown in Figure 3.4b. It was observed that the thin TiO₂ coating did not affect the leakage current in the low leakage range a lot. More specifically, the average I_{TG} of the TiO₂-coated and bare graphene devices shown in Figure 3.4b were found to be ~ 2.18nA and 11nA, respectively, at $V_{TG} = +0.2V$. The defect density of the graphene and the coverage of TiO₂ affects the leakage current considerably, and as a result, the difference in I_{TG} for bare and TiO₂-coated graphene in the low leakage range had a high variance, sometimes being almost same for both devices. Thus it can be concluded that such a thin layer of TiO_2 (3 nm) does not affect leakage current significantly in graphene devices.



3.2.4 Leakage Current in Membranes with Nanopores

Figure 3.5: (a) TEM image of a 3.3 nm nanopore in a 3 nm TiO_2 covered graphene membrane. (b) Device and circuit schematic of gating setup to measure leakage current in a nanopore device. Red and blue arrows show current directions for a relative positive and negative driving bias voltages, respectively, between bottom electrode and graphene.

Nanopores were drilled in the TiO_2 -coated suspended graphene membrane with transmission electron beam ablation lithography (TEBAL) [50] in JEOL 2010F TEM ranging in diameter from 3 nm to 10 nm (Figure 3.5a). 15 minutes UV-ozone treatment was performed on the nanopores to help wet the pore using NovaScan PSD-UV Ozone Cleaner. [121]

Gating setup for the device and the corresponding simplified current schematic are shown in Figure 3.5b. The graphene voltage (V_{gr}) acts as the gate voltage for the ionic current flowing through the nanopore (I_{pore}) due to the driving bias voltage between the top and bottom electrodes (V_{TB}) . But application of a voltage to graphene also introduces leakage currents between the graphene and the top (I_{TG}) and bottom (I_{BG}) electrodes. I_{pore} can be considered to be a linear combination of total measured current between the top and bottom electrode (I_{TB}) and the leakage currents during relative positive driving bias voltage with respect to graphene:

$$I_{pore} = I_{TB} - I_{BG} \tag{3.1}$$

and relative negative driving bias voltage with respect to graphene:

$$I_{pore} = I_{TB} - I_{TG} \tag{3.2}$$

To be able to see gating effect of V_{gr} on I_{pore} , the leakage currents should be such that:

$$I_{BG}, I_{TG} \ll I_{pore} \tag{3.3}$$

for the total voltage range of the gating measurement.

A 5.1 nm nanopore (Figure 3.6b(inset)) was drilled in a graphene membrane coated on both sides with 3 nm TiO₂ and was subjected to 15 min UV-ozone irradiation to wet the pore. The graphene sheet resistance was measured before and after UV-ozone treatment and found to be the ~ 2.5 k Ω /sq for both cases. The ionic conductance curve of the pore was obtained for 1M KCl for V_{pore} = ±0.5 V and no graphene bias (Figure 3.6a). The open pore conductance (G) was found from the slope of the curve



Figure 3.6: (a) Device schematic for measurement of open pore conductance of a TiO_2 coated graphene nanopore. (b) Open pore conductance of the a 5.1 nm diameter nanopore in 1M KCl. (inset) TEM image of the nanopore.

to be ~ 67 nS (Figure 3.6b). The pore conductance (G) was calculated from the geometric pore equation [82]:

$$G = \sigma \left(\frac{4L}{\pi d^2} + \frac{1}{d}\right)^{-1} \tag{3.4}$$

using measured pore diameter (d) = 5.1 nm, solution conductivity (σ) = 11.11 S/m and assumed pore thickness (L) = 7 nm (considering ~ 1 nm thick graphene membrane sandwiched between two 3 nm thick TiO₂ layers) and found to be ~ 21 nS, nearly 0.3 times the measured conductance value. This mismatch in pore conductance can arise due to a variety of factors. Formation of pinholes is possible during TEBAL and UV-irradiation step leading to parallel ion channels through the membrane, thereby increasing open pore conductance. [121] Thinning of the membrane in the vicinity of the nanopore while TEM drilling [146] and the presence of an intrinsic surface charge density in the nanopore [160] can also contribute towards higher measured conductance.



Figure 3.7: (a) Device schematic for measurement of leakage current between graphene and bottom electrode of a TiO_2 coated graphene nanopore. (b) Bottom leakage current measurement and (inset) comparison with the top leakage current for the same device.

Bottom side leakage current (I_{BG}) was measured on the wet nanopore for 1M KCl by sweeping bottom-to-graphene voltage (V_{BG}) from -0.3 V to +0.5 V at dV/dt = 20 mV/s, the setup of which is shown in Figure 3.7a. The leakage trend (I_{BG} vs. V_{BG}) obtained (Figure 3.7b) was similar to top-side leakage curve at the same sweep rate (20 mV/s) but the average I_{BG} in the low leakage range and I_{peak} for bottom leakage were comparatively smaller than the I_{TG} measured for the same device (Figure 3.7b(inset)), suggesting higher reaction resistance and lower capacitance for bottom side. The average I_{TG} and I_{BG} were 6.36 nA and 0.96 nA, respectively, at graphene voltage of +0.2V and dV/dt = 20 mV/s, which corresponds to a nearly 6-fold decrease in leakage current magnitude. This suggests that the area of interaction between the graphene and the electrolyte plays a major role in leakage. As the area of the graphene membrane in contact with KCl solution is smaller for bottom side leakage setup (which is equal to the region suspended over the FIB hole ~ 0.3 μ m²), it is expected that both the number of active sites interacting with the electrolyte and the EDL capacitance area is much lower when compared to the total exposed graphene area on the top side (~ 0.2 mm²).

We define the low bottom leakage region for our device in the voltage range -0.18 $V < V_{BG} < +0.36$ V such that average $|I_{BG}| < 2$ nA. We would expect to see linear trend for top-to-bottom ionic curve (I_{TB} vs. V_{TB}) in this graphene gate voltage range, as the leakage current will be comparatively less than the pore current (Figure 3.6).

3.2.5 Gating Measurements



Figure 3.8: (a) Current-voltage measurement of total ionic current (I_{TB}) with nanopore driving bias voltage (V_{TB}) through a TiO₂ covered graphene nanopore for different graphene gate voltages (V_{gr}) . (b) Extracted conductance graphs in nanopore driving bias voltage range with least leakage current. (inset) Change in conductance as a function of graphene voltage.

Gating measurements were performed on the device by applying a fixed graphene gate voltage (V_{gr}) and sweeping the top-to-bottom driving bias voltage (V_{TB}) across the membrane (Figure 3.8a). As mentioned before, the current obtained through the nanopore as a result (I_{TB}) is a linear combination of the I_{pore} and leakage currents ($I_{BG} \& I_{TG}$). V_{TB} was varied from -0.5V to +0.5V while V_{gr} was kept constant at -0.2V, -0.1V and +0.1V. It must be noted that the graphene voltage (V_{gr}) is different from bottom-to-graphene voltage (V_{BG}). For this setup, the top electrode is kept at ground (Figure 3.5b) while a constant V_{gr} is applied to the graphene and V_{TB} sweep is applied to the bottom electrode. The difference of these two voltages gives us V_{BG} :

$$V_{BG} = V_{gr} - V_{TB} \tag{3.5}$$

As V_{gr} remains constant during a sweep, the top-to-graphene voltage (V_{TG}) on the other hand is given simply by:

$$V_{TG} = V_{gr} \tag{3.6}$$

It can be seen from Figure 3.8a that when V_{BG} approaches high leakage region $(+0.36 \text{ V} < (V_{gr} - V_{TB}) < -0.18 \text{ V})$, I_{BG} dominates I_{pore} and non-linear trend is seen in the I_{TB} vs. V_{TB} for all V_{gr} . It should be noted here that V_{TG} (= V_{gr}) was kept < -0.2 V to maintain a constant low leakage current between the top electrode and graphene, as determined previously.

To observe gating effects of V_{gr} , we extract I_{TB} for V_{BG} in the range of -0.18 V and +0.36 V for all measured V_{gr} curves (Figure 3.8b). The corresponding portion for $V_{gr} = +0.1$ V is shown with green cut lines in Figure 3.8a. The conductance for each curve was measured and plotted as a function of V_{gr} (Figure 3.8b(inset)). The trend obtained was that of a linearly decreasing open pore conductance with increase in graphene voltage.

To understand this trend we have to understand the role of EDL at the grapheneelectrolyte interface in gating of the nanopore. The ionic channel in the nanopore has two regions - one central bulk ionic region and a Debye layer on the nanopore walls/edges due to the surface charge density of the pore. Taking into consideration both the geometrical factor and the surface charge density factor for a nanopore, the pore conductance is given by [160]:

$$G = \sigma \left(\frac{4L}{\pi d^2} + \frac{1}{d}\right)^{-1} + \frac{\pi d |\sigma_{surf}|}{L} \mu_{cti}$$

$$(3.7)$$

where σ_{surf} is the surface charge density of the pore walls and μ_{cti} is the electrophoretic mobility of the counterions in the EDL. When a potential is applied to the graphene membrane, the counterion density around the pore changes in order to nullify the change in the surface charge of the pore. This changes the second term in the above equation, thereby changing the overall pore conductance. [153]

Decreasing pore conductance with increasing graphene voltage could mean that the graphene pore has an intrinsic negative surface charge density. Application of a negative bias increases the counterion (K^+ ion) concentration further, thereby increasing ionic current through the pore, whereas increase in graphene voltage reduces the number of counterions and bring its concentration closer to bulk and decrease in ionic current. This also explains why we see a higher open pore conductance than expected for a pore size seen in TEM. Presence of hanging bonds at the graphene defect sites (introduced during growth [134] and by UV-ozone oxidation [121]) can lead to formation of -H and -OH groups in solution, thereby introducing an overall negative surface charge density to the graphene membrane. [26, 57, 190]

As the Debye length (λ_D) for 1M KCl at room temperature is only 0.3 nm thick (~ 6% the diameter of the pore), application of voltage to graphene is not expected to significantly modulate I_{pore}. [127, 174] Indeed, little change in open pore conductance (slope of IV curve ~ 75 nS/V) was seen in the safe region. At high pore biases the graphene starts to operate in the high leakage region and high I_{pore} was seen. To observe significant gating effects, the molarity of the solution should be reduced such that the λ_D increases and I_{pore} has higher contribution from the ions in the Debye layer.

3.2.6 Conclusion

In conclusion, we investigated the various factors that influence gating control in thin graphene nanopores. It was determined that V_{gr} should be applied such that the potential difference between graphene and either electrodes remains within the low leakage range, which was found out to be in the range -0.2 V to +0.4 V for graphene and Ag/AgCl electrodes in 1M KCl. To further reduce the effect of leakage on ionic current, the area of graphene exposed to the electrolyte should be kept at a minimum. Gating was observed in TiO₂ covered graphene nanopore, but as the Debye length was too small (~ 6% of our nanopore diameter) for 1M KCl, gating effect was not significant (~ 75 nS/V). Future studies may focus on investigating gating and local control of DNA by tuning these parameters in graphene nanopores to reduce leakage current while increasing ionic signal strength and gating control.
3.3 Laser-Induced Modulation of WS₂ Nanopores

The results presented here were published in the article "Monolayer WS₂ Nanopores for DNA Translocation with Light-Adjustable Sizes" by Danda, G., Masih Das, P., Chou, Y.C., Mlack, J.T., Parkin, W.M., Naylor, C.H., Fujisawa, K., Zhang, T., Fulton, L.B., Terrones, M., Johnson, A.T.C., and Drndić, M., ACS nano, 11(2), pp.1937-1945 (2017).

3.3.1 Background

Nanopore sensors based on two-dimensional (2D) materials such as graphene, molybdenum disulfide (MoS_2) and boron nitride (BN) have been used to demonstrate biomolecule detection and analysis. [47, 56, 103, 121, 152, 209] In these experiments, the molecules, suspended in an ionic solution, are driven by an electric field through a nanopore within a thin membrane while the ionic current is monitored to detect the translocation of molecules across the nanopore, which typically appears as reductions in current. Atomically thin 2D membranes are ideal for nanopore devices as they exhibit larger ionic currents compared to thicker silicon-based membranes [47, 56, 103, 121, 152, 209] and potential spatial sensitivity at the sub-nanometer scale for translocating molecules as only a small section of the molecule resides in the nanopore at a given time. [56] Furthermore, monolayers of semiconducting transition metal dichalcogenides (TMDs) possess enhanced optical properties, [64, 75, 137] a feature which could be further exploited for electrical and optical control of nanopores.

Among TMDs, monolayer tungsten disulfide (WS_2) has a direct band gap of 2.1 eV

[11] and its photoluminescence (PL) emission is stronger than the well-studied MoS_2 , [137, 199] which enables application of WS_2 monolayers in optoelectronic devices. [70] It is also noteworthy that defects have been shown to modulate the PL signal of WS_2 monolayer flakes [24, 169] and can hence be used as a means to fine tune their optical response. One related property is the photo-oxidation of TMD monolayers in an oxidizing environment, like air and water. [2, 53] Introducing defects in the material can provide sites for light-facilitated oxidation and can be used to dynamically control defect size using optical excitation.

In this section, a class of optically active 2D nanopores in monolayer WS₂ membranes is demonstrated. WS₂ nanopore drilling using a focused electron beam and subsequent effects on PL spectra are reported. High ionic conductance and DNA translocations through these nanopores are also obtained. Furthermore, during laser excitation of these nanopores at low power densities ($\lambda = 532$ nm, power density $= 3 \text{ W/cm}^2$), nanopore expansion at a rate of ~ 0.2-0.4 nm/s is seen, potentially providing means to dynamically control nanopore dimensions with short light pulses.

3.3.2 Flake Characterization

Figure 3.9 shows the material characterization of WS₂ triangular monolayers grown using chemical vapor deposition by our collaborators at University of Pennsylvania and Pennsylvania State University. Atomic force microscopy (AFM) of the flake (Figure 3.9b) shown in Figure 3.9a reveals a thickness of ~ 0.7 nm, which agrees with the reported thickness of monolayer WS₂. [164] Using Raman spectroscopy, the E' (353 cm⁻¹) and A₁' (418 cm⁻¹) modes of monolayer WS₂ as well as the Si peak from



Figure 3.9: (a) Optical micrograph and (b) AFM scan of a monolayer WS2 flake. The line profile in white indicates a thickness of 0.7 nm, which corresponds to a monolayer. (c) Raman spectrum of monolayer WS₂ flake with corresponding E' (356 cm⁻¹), A_1 ' (418 cm⁻¹), and Si (521 cm⁻¹) peaks. (d) Gaussian blur-filtered AC-HRSTEM lattice image taken at 80 kV. The inset is a SAED pattern with expected (100) and (110) diffraction spots.

the substrate centered at 521 cm⁻¹ were observed (Figure 3.9c). [164] The peak at 311 cm^{-1} that is typically associated with multilayer flakes is notably absent, [205] thus confirming the presence of monolayers. Figure 3.9d is an aberration-corrected high-resolution scanning transmission electron microscope (AC-HRSTEM) image of a freestanding WS₂ monolayer suspended on a perforated carbon grid. The tungsten (bright white) and sulfur (gray) atoms are clearly visible. Selected-area electron diffraction (SAED) patterns (inset) also confirmed the expected hexagonal lattice of the 1H phase of WS₂ monolayers.

We further characterize the WS_2 monolayers using PL spectroscopy. WS_2 flakes were suspended onto a perforated silicon nitride grid (DuraSiN DTM-25231) using a standard PMMA-based wet transfer procedure (Figure 3.10a) and PL spectral maps were obtained using a 532 nm laser excitation (Figure 3.10b). The PL spectra from various regions of the flake - suspended, supported edge and supported center - are



Figure 3.10: (a) Optical image of monolayer WS₂ flake on a perforated silicon nitride grid, outlined in red, and (b) corresponding PL map with a 532 nm laser. PL spectra for suspended (black dot), supported edge (red dot), and supported center (blue dot) are plotted in (c). The neutral exciton peak, X₀, at ~ 2.02 eV, trion peak, X_T, at ~ 1.98 eV, and defect peak, X_D, at ~ 1.88 eV are shown with dotted lines. The edge (red) and center (blue) spectra are multiplied by a factor of 4 for better illustration.

plotted in Figure 3.10c. The PL signal exhibited 3 peaks: (i) the neutral exciton peak (X_0) , which arises due to the radiative recombination of excitons across the bandgap, [24, 182, 206] (ii) the charged trion peak (X_T) , which comes from the recombination process requiring three charge carriers and as a result can arise due to charge doping [23, 75, 143] or strain, [181] and (iii) defect peaks (X_D) , which arise due to defect-induced midgap states that allow excitons to recombine at an energy lower than the bandgap. [24, 169] Lorentzian functions were used to fit the spectra for X_0 , X_T and X_D peaks. It was observed that the X_0 peak centered at ~ 2.02 eV red shifts (*i.e.*, PL wavelength increases) and decreases in intensity (or peak area) from the flake edge inwards until it becomes completely non-existent at the center of the flake. On

the other hand, the X_T peak shifts from 1.98 eV to 1.94 eV (*i.e.*, red shifts) and the peak intensity decreases by 3 times from edge of the flake to inner region. [75] The presence of the X_T peak lends the low energy tail in the spectra and likely appears due to the substrate-induced strain in the transferred flake. [30] The enhancement of the PL spectral intensity was observed between the suspended and the nearby supported region, which was measured as the ratio of the X_0 peak intensity (I_{sus}/I_{sup}), to be ~ 10-15 times, irrespective of the position of the suspended region on the monolayer (*i.e.*, edge or center). This effect has previously been observed and quantified in suspended MoS₂ monolayers where the enhancement was ~ 2-4 times [150] and was attributed to PL quenching caused by charge doping of the substrate in the supported regions. Similar effects have been observed in suspended WS₂ [75] but were not quantified, to the best of our knowledge.

3.3.3 Effect of Electron-Beam Damage on PL

Before drilling a nanopore in a suspended region of a WS₂ flake, the position of the suspended region must first be located in the TEM, and as a result the entire suspended region is exposed to electron beam (e-beam) doses on the order of ~ 10^4 - $10^5 \text{ e}^-/\text{nm}^2$. It has been established that high energy e-beams can introduce lattice defects in TMDs (such as sulfur vacancies in MoS₂ [135]) and in other 2D materials. [144] These defects can in turn cause changes in PL peak intensities due to trapped charge carriers, or introduce additional peaks as a result of the creation of midgap states. [24, 75, 137, 169] Thus, it is advantageous to study the effects of e-beam exposure on the PL of suspended WS₂ monolayers during nanopore drilling.



Figure 3.11: PL intensity maps of flakes (a,d) before and (b,e) after STEM drilling with dose = 2.6×10^5 and 5.5×10^4 e⁻/nm², respectively. (c,f) PL of the suspended regions, marked with blue arrows in (a,b) and (d,e), respectively, before and after STEM drilling. (Insets) STEM images of the drilled nanopores. Yellow dotted lines in (b, e) show regions damaged during STEM imaging. Both suspended regions have 2-3 nanopores (diameter ≤ 10 nm).

We observe a change in the intensity of PL signals and formation of additional defect peaks due to imaging and nanopore drilling in STEM mode with different ebeam doses. Prior to imaging, the samples were subjected to rapid thermal annealing at 300°C for 90 mins in H₂/Ar in order to reduce any carbon contamination during drilling. [144] PL maps of two different WS₂ flakes were obtained before (Figures 3.11a, 3.11d) and after e-beam drilling (Figure 3.11b - dose A = $2.6 \times 10^5 \text{ e}^-/\text{nm}^2$, Figure 3.11e - dose $B = 5.5 \times 10^4 \text{ e}^{-}/\text{nm}^2$) in the suspended region marked with a blue arrow. After undergoing 3-4 minutes of e-beam exposure (STEM imaging), 2-3 nanopores with diameters ~ 10 nm each were drilled in focused-spot mode in both membranes in close vicinity, as shown in the insets of Figures 3.11c and 3.11f. The nanopores were drilled close to each other (< 0.5 μ m apart) to roughly differentiate between effects arising from beam exposure versus nanopore drilling, as we were limited by lateral PL resolution of 0.5 μ m. As can be seen from Figures 3.11b and 3.11e, the beam exposure is clearly visible in the PL map as a darker region around the suspended region (outlined in yellow), with more widespread damage from dose A rather than from dose B.

The PL spectrum of the suspended membrane shown in Figure 3.11c reveals that imaging with dose A resulted in the quenching of the X₀ (neutral exciton) peak, a ~ 26-fold decrease of the X_T (charged trion) peak and a ~ 2-fold increase of the X_D (defect) peak at ~ 1.85 eV. On the other hand, dose B (Figure 3.11f) led to almost no change of the X₀ and X_T peak intensities in addition to the formation of an additional X_D peak located at ~ 1.87 eV, which was initially absent for this flake. It should be noted that these spectra are obtained from the suspended region exposed only to the e-beam (R_{BE}) and not subjected to drilling (R_{NP}), which is studied next. These changes take place due to the e-beam bombardment damage that occurs during STEM imaging, which leads to sulfur vacancies and other defects with densities proportional to the e-beam dose. [135, 144]

To differentiate the effects due to beam exposure from those of nanopore drilling, we recorded PL maps of the suspended membrane near the nanopores, before (Figure



Figure 3.12: PL intensity maps of the zoomed-in suspended region of the flake shown in 3.11(d,e) before (a) and after (b) drilling, showing nanopore-induced PL change in the area outlined in blue (R_{NP}). (c) PL of the R_{NP} , marked with a blue dot in (a,b) before and after drilling.

3.12a) and after (Figure 3.12b) drilling and found variations in the PL intensity across the monolayer membrane. Although the entire suspended region was exposed to the scanning beam during imaging in STEM mode, a darker region to the right of the membrane (R_{NP} ; outlined in blue; diameter ~ 0.6 μ m) was observed where the nanopores were drilled while the left side of the membrane was relatively unaffected (R_{BE}). R_{NP} showed a 2-fold decrease in both the X₀ and X_T peak intensities and the formation of the X_D peak at ~ 1.88 eV (Figure 3.12c). The spectral weight percentage (*i.e.*, intensity percentage) of X_D differed in the two regions, with 10% for R_{BE} and 47% for R_{NP} , thus showing higher density of defects occurring near the nanopore. It was also observed that while the enhancement factor (I_{sus}/I_{sup}) remained ~ 12 for R_{BE} , R_{NP} had a reduced enhancement factor of ~ 6. The defects introduced due to the nanopore drilling in the vicinity of R_{NP} can provide sites for oxidation, which we investigate later in our report. It should be noted that the laser exposure from PL and Raman measurements was not seen to introduce additional defects. This was verified by letting the focused laser beam (power density = $4.4 \times 10^4 \text{ W/cm}^2$) illuminate suspended WS₂ regions (both with and without a nanopore) for at least 5 minutes. Raman measurements, from before and after exposure, also indicated no measurable change or shift in the WS₂ spectrum.

3.3.4 Nanopore Device Characterization



Figure 3.13: (a) Schematic of the nanopore device setup. (b) Optical image of a triangular WS₂ flake on a SiN_x window with a FIB hole. (Inset) Scanning electron microscopy image of a 300 nm FIB hole. (c) AC-HRSTEM image of (i) an undamaged suspended WS₂ membrane, (ii) a 0.3 nm nanopore, and (iii) a 1.3 nm nanopore drilled with accelerating voltage of 80 kV. (d) Plot of open pore conductance of WS₂ nanopores with the corresponding nanopore diameter. Inset shows the plot over a larger d_{TEM} range.

A schematic of a typical WS₂ nanopore device is shown in Figure 3.13a. 50-nmthick suspended silicon nitride (SiN_x) membranes with dimension 50 μ m x 50 μ m were fabricated on 5 μ m/500 μ m SiO₂/Si wafers using optical lithography. [121, 176] A 200-500 nm diameter hole (area = 0.03 - 0.2 μ m²) was drilled in the SiN_x membrane using a focused ion beam (FIB) with a 10 pA, 30 kV Ga⁺ source, as illustrated in Figure 3.13b (inset). Monolayers of WS₂ were transferred onto the SiN_x membrane using either a Kapton tape-based micromanipulation positioning technique or a PMMAbased wet transfer procedure. A successful transfer is shown in Figure 3.13b. Using the focused STEM probe with dose B, nanopores of diameters ranging from 2 to 8 nm were then drilled in the WS₂ membranes suspended over the FIB holes. AC-HRSTEM images of similarly drilled nanopores are illustrated in Figure 3.13c.

After loading onto a PDMS measurement cell, the nanopore device was wet using an ethanol:water (v/v 1:1) solution, [103] after which the electrolyte solution was introduced on both sides of the device. A bias voltage sweep (V_B) was applied across the membrane and the ionic current (I_B) through the nanopore was monitored using a current amplifier in order to obtain the open pore conductance (G₀ = I_B/V_B). 1 M KCl solution was used as the electrolyte for most of our experiments, unless otherwise noted. G₀ was plotted with the measured nanopore diameter (d_{TEM}) for several nanopore devices (see Figure 3.13d). By fitting the graph to a linear function, solution conductivity was calculated to be 13.5 ± 0.3 S/m, in good agreement with the measured conductivity of 11.8 S/m, using the conductance formula for 2D nanopores:

$$G_0 = \sigma d_{TEM} \tag{3.8}$$

where G_0 is the open pore conductance, σ is the calculated solution conductivity and d_{TEM} is the diameter of the nanopore measured from the corresponding STEM image. [152]

3.3.5 DNA Translocation Experiments



Figure 3.14: (a) Current-voltage measurement of WS₂ nanopores with diameters (d_{TEM}) of (i) 4.4 ± 0.9 nm (pore A in red) and (ii) 7.1 ± 0.5 nm (pore B in black), yielding open pore conductances of 61.01 nS and 69.86 nS, respectively. (b) Ionic conductance time trace of DNA translocation events through the nanopore devices shown in (a) with 10 ng/µL of 15 kbp dsDNA at $V_B = 400$ mV for pore A and $V_B = 200$ mV for pore B filtered at 10 kHz. (c) Zoomed-in events illustrating unfolded, partially folded, and folded (left to right) DNA translocation events with the open pore conductance subtracted for pore A.

Open pore conductances for WS₂ nanopores with (i) $d_{TEM} = 4.4 \pm 0.9$ nm (pore A - red) and (ii) $d_{TEM} = 7.1 \pm 0.5$ nm (pore B - black) were obtained by cycling V_B between \pm 200 mV (Figure 3.14a). It should be noted that 3 M and 1 M KCl solutions were used for pore A and pore B, respectively. The G₀ values thus obtained were 61.01 nS for pore A and 69.86 nS for pore B.

15 kbp double stranded DNA (10 ng/ μ l, random sequence) in buffered KCl solution was then introduced into the *cis* chamber and a constant V_B (400 mV for pore A and 200 mV for pore B) was applied to electrophoretically drive the DNA through the nanopore. The current traces hence obtained show DNA translocation events (see Figure 3.14b). We use the change in conductance ($\Delta G = \Delta I_B/V_B$) instead of change in ionic current to normalize our results. As pore diameters here are ~ 2-3 times larger than the diameter of dsDNA (~ 2.1 nm), we observe events that can be interpreted as DNA translocating in 3 possible orientations - unfolded, partially folded, and folded - each resulting in different current blockage levels (Figure 3.14c). [123] We note that folded DNA translocation events in 3 M KCl have been reported in graphene and silicon nitride nanopores down to ~ 4.0 nm. [56, 123]



Figure 3.15: Scatter plots of change in conductance vs event duration for 1890 events (pore A). The histogram on the right shows the change in conductance fitted with two Gaussian curves for unfolded (ΔG_u , yellow) and folded events (ΔG_f , cyan). The histogram on the top shows the event duration or dwell time fitted with two exponential decay curves for unfolded (τ_u) and folded (τ_f) events.

Scatter plots of (i) 1890 events and (ii) 2030 events were obtained from pores A and B, respectively, and the corresponding histograms of the event depths (change in conductance or ΔG) and dwell time (duration of events) are plotted in Figures 3.15 and 3.16, respectively. As partially folded events may have various degrees of folding depending on the percentage of overlap, one distinct Gaussian distribution might not be representative of all the possible partially folded translocations. As a result, the event depth histograms were fitted to only two Gaussian curves which correspond to unfolded events (ΔG_u represented by the yellow curve) and folded events (ΔG_f represented by the cyan curve). Average change in conductances of (i) $\Delta G_u = 13.26$ nS and $\Delta G_f = 25.44$ nS for pore A, and (ii) $\Delta G_u = 2.62$ nS and $\Delta G_f = 4.41$ nS for pore B were obtained, yielding unfolded translocation blockage percentages ($\Delta G_u/G_0$) of ~ 22% and ~ 4% for pores A and B, respectively. These compare well with previously reported 2D nanopores. [103, 121, 209]

It is also common to fit the dwell time histogram to two exponential decay functions, one for unfolded events (τ_u) and one for folded events (τ_f). [121] In this case, we obtain time constants of (i) $\tau_u \sim 620 \ \mu$ s and $\tau_f \sim 100 \ \mu$ s for pore A and (ii) $\tau_u \sim 80 \ \mu$ s for pore B. τ_f was not obtained for pore B due to limitations in the sampling rate (50 kHz) of our current amplifier. High KCl concentration has been shown to reduce DNA-graphene interactions [55] and lead to shorter dwell times for folded ds-DNA translocation events. [56] It is likely that a similar mechanism is happening in pore A.



Figure 3.16: Scatter plots of change in conductance vs event duration for 2030 events (pore B). The histogram on the right shows the change in conductance fitted with two Gaussian curves for unfolded (ΔG_u , yellow) and folded events (ΔG_f , cyan). The histogram on the top shows the event duration or dwell time fitted with one exponential decay curve for unfolded (τ_u) events.

3.3.6 Laser Irradiation of TMD Nanopores

Samples were illuminated using a 532 nm (green) excitation laser (Laserglow Technologies) with a 5 mW power output. Power density was controlled by changing the laser driving current and via a variable neutral density filter (Thorlabs), and calibrated with a PHIR power meter located at the sample stage. All cables were kept electrically isolated or grounded to reduce any cross-talk. Alignment was performed by first focusing the laser on a white piece of paper and observing it using the CMOS camera. The laser spot was then centered and digitally marked in the image capture software window by changing the mirror orientations. This spot was then aligned to the nanopore device windows mounted on the micromanipulator stage with the laser beam turned off.



Figure 3.17: (a) Schematic of the optical measurement setup. (b) Change in ionic current through WS₂ and SiN_x nanopores with laser exposure. Ionic current measurements at $V_B = 100$ mV were obtained for two WS₂ nanopores of effective diameters of (i) 11.1 nm (pore C) and (ii) 43.2 nm (pore D) and a SiN_x nanopore with (iii) $d_{eff} = 4.8$ nm. Periods when the laser is turned on (light) and off (dark) are represented in green and black, respectively.

In addition to ionic current measurements in the dark, we also applied light to the nanopores to quantify the ionic current under illumination and explore the optical response of monolayer WS₂ nanopores in a biased ionic environment. The measurement setup is illustrated in Figure 3.17a. By means of a CMOS camera and a 4X objective lens (NA = 0.1), a 532 nm wavelength laser was monitored and focused on WS₂ nanopore devices mounted on a 3-axis micromanipulator stage. The power

density of the laser was changed via a variable neutral density filter and by varying the laser driving current, both of which were calibrated using a power meter.

In order to understand the effect of light on a WS₂ nanopore in an ionic solution, the pore conductance of multiple devices was measured as a function of laser exposure time. Here, we show results for a WS₂ nanopore (pore C) with an effective diameter $(d_e ff = G/\sigma)$ of 11.5 nm. As illustrated in Figure 3.17b (i), I_B was monitored at a constant V_B = 100 mV while the laser was turned on and off alternately with a constant power density of 3 W/cm². Before exposure, the pore conductance in the dark was stable over a period of 1 hour. However, during laser exposure, the I_B was seen to increase (green) and remained constant when the laser was turned off (black). This seemed to be an irreversible effect, resulting in ionic current time-traces consisting of a series of constant current periods (in the dark) connected by periods of increasing current (under laser illumination).

Membrane charging cannot explain these observations, which would otherwise exhibit a return to the original conductance upon dissipation. [42] We instead attribute it to a permanent physical expansion of the nanopore, confirmed by STEM imaging of nanopores, as discussed later on. A similar result was obtained for (ii) another WS₂ nanopore (pore D - $d_{eff} = 43.2$ nm) under the same voltage and power density conditions. However, this was not the case for (iii) a SiN_x nanopore ($d_{eff} = 4.8$ nm), which showed no change in ionic current as a function of laser exposure at the same power density. This important control measurement demonstrates that solution evaporation and/or solution heating is also not the responsible mechanism for our observation, as either or both could cause a variation in ionic current regardless of the nanopore

membrane material. It should be noted that enhancement of ionic current through a SiN_x nanopore has been reported previously, but at power densities ~ 6 orders of magnitude higher than what is used here. [42]



Figure 3.18: (a) Change in effective diameter of pore C with time. The regions with the laser on (green) were extracted and concatenated into a single plot (inset) as a function of exposure time, t_L . An illustration of the expansion of the pore is shown on the top left. (b) STEM observation of the laser-induced expansion of nanopores with initial diameters (d_{TEM}) of (i) 4.6, (iii) 4.0, and (v) 4.0 nm at power densities of (ii) 5400, (iv) 90, and (vi) 3 W/cm² and $V_B = 0$ V.

The observed nanopore expansion was further characterized by calculating the change in the effective nanopore diameter throughout the experiment for pore C (Figure 3.18a). The regions when the pore was exposed to light (green) were extracted and concatenated (Figure 3.18a inset) to help understand how d_{eff} changes with

the laser exposure time (t_L) . The d_{eff} vs. t_L plot was best fit empirically to an exponential trend:

$$d_{eff}(t_L) \sim \alpha - \beta e^{(-t_L/\gamma)} \tag{3.9}$$

where $\alpha = 55.1$ nm, $\beta = 43.6$ nm and $\gamma = 249.5$ s. The rate of expansion of the nanopore can then be calculated as:

$$\frac{\delta[d_{eff}(t_L)]}{\delta t_L} \sim \beta / \gamma e^{(-t_L/\gamma)} \tag{3.10}$$

where β/γ is the initial rate of expansion of pore. For pore C, this value was calculated to be 0.2 nm/s while for pore D it was 0.4 nm/s. The approximate initial expansion rate was also calculated for other power densities by measuring the conductance change due to exposure of $t_L = 5$ s. It was seen that the expansion rate increased as the laser power density increased. It should be noted here that to ensure that the low $V_B = 100$ mV did not affect the nanopore, conductance was measured and seen to be constant for an hour in the dark. Nanopore illumination was also repeated with $V_B = 0$ V and conductance was measured in the dark after illumination, resulting in similar outcomes to those presented here.

To gain a better understanding of how nanopore expansion varies with power density, three nanopores were subjected to different power densities for $t_L = 5$ s and observed under STEM. In all cases, we measured the conductance before and after exposure. After the ionic measurement, the membrane was rinsed from the salt solution with water and annealed to allow for subsequent STEM imaging. Figure 3.18b shows STEM images of WS₂ nanopores with $d_{TEM} = 4.6 \text{ nm}$ (i) before and (ii) after being exposed to a power density 5400 W/cm², $d_{TEM} = 4.0 \text{ nm}$ (iii) before and (iv) after being exposed to a power density of 90 W/cm², and $d_{TEM} = 4.0 \text{ nm}$ (v) before and (vi) after being exposed to power density of 3 W/cm². While the highest power density physically breaks the suspended membrane completely, the lower power densities gradually increases the pore size. This is also evident from the measured change in pore conductances, which increased by ~ 1275 nS for a power density of 5400 W/cm², by ~ 592 nS for 90 W/cm², and by ~ 39 nS for 3 W/cm². It is possible in some cases to find other pre-existing pores in the membranes that can further grow due to e-beam exposure during STEM imaging.

Even though we see irregular pore shape growth for large light intensities (90 W/cm^2), we see steadier and more controlled expansion at lower light intensities (3 W/cm^2) as shown in Figure 3.18b. By further optimization of this process, the use of controlled light pulses with controlled intensity and duration, it may be possible to make this process highly controllable and usable for applications. This is somewhat analogous to recently developed membrane electroporation protocols using voltage pulses. [85, 86, 191] While these voltage pulses can break the membrane at high voltage and long durations, the procedure have been optimized for nanopore formation by fine control of the magnitude and duration of the pulses.

We also explored the impact of laser exposure on intact suspended WS₂ membranes containing no e-beam drilled nanopores. A rectifying curve is obtained initially with $G_0 = 2$ nS (corresponding to $d_{eff} = 0.2$ nm) possibly indicating the presence of intrinsic sub-nm pinholes in the membrane (Figure 3.19). Upon laser exposure



Figure 3.19: IV curves were obtained before and after laser exposure (power density of 90 W/cm², $t_L = 15$ s) on an intact WS₂ membrane containing no nanopores. The observed increase in conductance, G₀, from 2 to 9 nS suggests that the laser aids in creating ionic channels through existing defects. Under additional exposure with a higher power density (power density ~ 5400 W/cm², $t_L = 6$ s), no increase in conductance was observed, indicating that exposed edges, such as those formed during e-beam nanopore drilling, are necessary to form larger channels.

(power density of 90 W/cm², $t_L = 15$ s), the conductance increased to 9 nS ($d_{eff} = 0.8$ nm). A further increase in power density (power density of 5400 W/cm², $t_L = 6$ s) did not increase the conductance or break the membrane. This seems to indicate that laser exposure might help form additional pathways for ionic flow if there are existing defects in the membranes. However, intentional e-beam damage used to create nanopores with exposed edges plays the dominant role in the further expansion of the nanopores upon illumination, and the ionic current through it is the major

contribution to the measured ionic current in nanopore devices.

Experiments were also conducted wherein suspended WS₂ membranes were exposed to STEM damage (dose = $1.1 \times 10^4 \text{ e}^-/\text{nm}^2$) without nanopore drilling, and laser illumination (power density of 90 W/cm², $t_L \sim 3$ mins) was applied to see if nanopores can be formed. No appreciable change in conductance was observed, suggesting no perceptible expansion of e-beam induced defects from the applied dose ranges. Further experiments are required to investigate the relation between e-beam dose, defect density and size, and the rate of defect formation and expansion in an ionic solution.

Based on our observations, we propose that e-beam induced defects of optimal size provide sites for photo-oxidation to take place in WS_2 membranes in an ionic solution, which generally occur at grain boundaries, [2, 53] leading to expansion of nanopores under laser illumination in KCl solution. Further studies are needed to explore the pore formation and expansion process in more detail and at the atomic scale using AC-HRSTEM characterization.

3.3.7 Conclusion

In this section, we presented the demonstration of optically responsive WS₂ nanopore sensors for biomolecule analysis. We characterized our vapor grown WS₂ monolayers using Raman spectroscopy, AFM, TEM imaging, and PL spectroscopy. We showed that imaging and drilling of nanopores using a focused e-beam can introduce defects in suspended WS₂ membranes, which appear as changes in the PL spectra. We determined a dose of $5.5 \times 10^4 \text{ e}^-/\text{nm}^2$ in STEM mode to be sufficient to drill a nanopore while adequately preserving the optical properties of WS₂ monolayers. Fabricated nanopore devices were then used to detect double-stranded DNA translocations. In contrast to SiN_x pores, the diameter of the WS₂ nanopore was optically expanded using a focused 532 nm laser, varying the rate of expansion as a function of incident optical power density. A rate of ~ 0.2-0.4 nm/s was obtained for a power density of 3 W/cm². We attribute this phenomenon to the photo-oxidation of nanopore edges in the ionic solution. We believe this initial study of WS₂ demonstrating electron beam induced effects on PL, DNA translocations through nanopores, and light-enabled pore expansion will aid future optoelectronic experiments on other optically-active TMD materials. Further studies may focus on understanding the detailed atomic mechanisms behind nanopore edges at atomic scales.

3.4 Summary

In this chapter, we realized nanopores in suspended graphene and monolayer WS_2 membranes, allowing for electrical and optical response in ionic current measurements. For the case of graphene nanopores, we observe that voltage application to graphene nanopores yield high leakage current at relative negative voltages suggesting high charge transfer between K⁺ ions and graphene. From this, we were able to extract a low leakage graphene voltage range and performed gating measurements in that range, observing a gating effect of ~ 75 nS/V. We also found that graphene exposure area plays an important role in leakage currents, and predict that using a low concentration

of electrolyte can increase gating control of ions.

For the case of WS₂ nanopores, we demonstrate their ability to detect DNA translocations with high sensitivity and also show that under low-power laser illumination in solution, the pores diameters can be controllably grown at an effective rate of ~ 0.2 -0.4 nm/s, thus allowing for future development of possible atomic-resolution pore size control using short light pulses. We follow-up on these results in our next set of experiments by studying the effect of laser irradiation on intact WS₂ membranes, as we will discuss in the next chapter.

Chapter 4

2D Nanoporous Membranes

4.1 Introduction

Two-dimensional nanoporous membranes are being studied as possible candidates for molecular filtration [1] applications due to predictions of high permeability and better ion selectivity. [26, 28] While graphene nanoporous devices have been demonstrated ion selectivity experimentally, [55, 69, 132, 165] no similar experiments using TMDs exist.

High vacuum techniques like ion irradiation and chemical/plasma etching are currently used to fabricate nanoporous 2D membranes, resulting in issues concerning scalability. As TMDs are known to be optochemically active, laser irradiation maybe used to fabricate nanoporous TMD membranes. In the first section of this chapter, we explore a new method for the fabrication of micron-scale, atomically-thin nanoporous tungsten disulfide (WS₂) membranes by utilizing water-assisted laser irradiation,. The electronic properties of the porous membranes are characterized with photoluminescence (PL) spectroscopy and the structural properties of defects are analyzed using aberration-corrected scanning transmission electron microscopy (AC-STEM), respectively. We also present a possible mechanism behind the observed laser-induced defects.

Nanoporous TMD membranes are predicted to have better permeability compared to graphene based on molecular dynamics (MD) studies, [66] but it has not been demonstrated experimentally as yet. In the second section of this chapter, we fabricate ion-irradiation induced Ångström size defects in intact, suspended molybdenum disulfide (MoS₂) membranes and demonstrate ion-selective transport via voltage driven ionic current through such pores. We also use MD modeling to find the minimum pore size for transport of K⁺ and Cl⁻ ions and compare the values to our experimentally obtained results.

4.2 Laser-Induced Fabrication of WS₂ Nanoporous Membranes

The results presented here were published in the article "Laser-Induced Fabrication of Nanoporous Monolayer WS₂ Membranes" by Danda, G., Masih Das, P., and Drndić, M., 2D materials (2018).

4.2.1 Background

Among the family of 2D materials, transition metal dichalcogenides (TMDs) have attracted a lot of attention as potential candidates for photodetection, [111, 166] purification, [159, 168] energy storage, [31, 162] and catalysis applications. [87, 203] Building upon the successful paradigm established by porous carbide-derived carbon (CDC) compounds in the latter application, porous TMDs and TMD-CDC hybrids have been heavily explored as possible electrocatalysts, [43] photocatalysts, [111, 210] and purification catalysts. [87, 203, 207] Despite their favorable performance, current fabrication techniques for porous TMDs based on solution-phase synthesis and solgel methods are primarily limited to relatively slow and energy-intensive recipes that either offer little to no tunability over sample porosity or fail to produce pore sizes below ~ 100 nm and fully utilize the 2D characteristics of the material. [87, 95, 210] Similarly, recently-reported methods for fabricating nanoporous molybdenum disulfide (MoS₂) based on ion beam patterning [52] and bottom-up molecular beam epitaxy (MBE) [207] seem promising but require a number of time-consuming processes, often under high-vacuum conditions that raise concerns over scalability. This necessitates the development of a process for the fabrication of TMDs with tunable porosity that is both rapid and scalable.

Owing to their direct semiconducting band gap and strong photoluminescence (PL) signature, monolayer TMDs have been probed for various optoelectronic applications such as phototransistors, [135, 194] light-emitting diodes, [149] and solar cells. [71, 157] Due to their strong optical absorption, the controlled layer-by-layer thinning of MoS₂ as well as the patterning of micron-scale holes in tungsten disulfide (WS₂) have also been achieved through laser-induced ablation. [19, 111] While the basal plane of monolayer flakes is known to be highly stable, intrinsic defects and edge sites have been shown to provide nucleation sites for this degradation process, [34, 136] which is accelerated in the presence of water. [2, 6, 136] These laser-induced defects, however, have not been observed at the atomic level and their study can provide more insight into the degradation process.

In this section, we demonstrate the controlled water-assisted photo-oxidation of pristine monolayer WS_2 membranes as a new method for producing nanopores and nanoporous TMDs with tunable porosity on the time scale of a few seconds. We analyze changes in the material's electronic structure through PL spectroscopy in addition to quantitatively and qualitatively characterizing the nature of the resulting porous structure using transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS).



Figure 4.1: (a) Optical image of CVD-grown monolayer WS_2 flakes on SiO₂. (b) Raman spectra of monolayer WS_2 flake with indicated primary modes. (c) SEM image of a WS_2 flake suspended on a holey carbon grid. (d) HAADF AC-STEM image of a monolayer WS_2 lattice taken at 80 kV. (inset) SAED pattern along the high-symmetry [001] zone axis showing the (100) and (110) diffraction spots.

4.2.2 Laser-Induced Defect Fabrication

Monolayer triangular WS₂ flakes are grown using a chemical vapor deposition (CVD) technique similar to that demonstrated by Kim *et al.* (2016). [75] We note here that the use of monolayer WS₂ arises from a combination of its highly-developed CVD growth techniques and exceptional room temperature PL properties in comparison to other TMDs. [64] Figure 4.1a shows an optical image of resulting triangular flakes on a 150 nm-thick SiO_2 substrate. The monolayer nature of the flakes was confirmed via Raman spectroscopy (Figure 4.1b) with an excitation wavelength of 532 nm. The Raman spectrum consists of the four primary modes - first-order in-plane acoustic mode, LA(M) (175 cm⁻¹), second-order in-plane acoustic mode, 2LA(M) (353 cm⁻¹), first-order in-plane optical mode, E' (Γ) (357 cm⁻¹), and first-order out-of-plane optical mode, A_1 ' (419 cm⁻¹) - and their derivative peaks. [13, 124, 139] The higher relative intensity of the 2LA(M) to A_1 ' mode and the absence of a prominent peak at $\sim 310 \text{ cm}^{-1}$ suggests the monolayer quality of the flake. [13, 205] However, to further verify that our flakes are in fact monolayer, we obtain PL spectra, as described later in the text. The flakes are transferred onto perforated carbon grids (perforation diameter $\sim 2.5~\mu{\rm m})$ using a standard PMMA-based KOH wet etch technique. A scanning electron microscope (SEM) image of a WS_2 flake suspended over multiple holes is shown in Figure 4.1c. Figure 4.1d shows a high-angle annular dark-field (HAADF) lattice image of a suspended region that was obtained in an aberration-corrected scanning transmission electron microscope (AC-STEM) along with (Figure 4.1d inset) a selected area electron diffraction (SAED) pattern.

Samples were irradiated with a laser using a custom-built illumination setup, as shown in Figure 4.2. Suspended WS₂ membranes were immersed in deionized (DI) water and located optically using a 60X water immersion objective lens and an integrated CMOS camera. A green laser ($\lambda = 532 \text{ nm}$, P = 5 mW) was then focused on selected membranes for an irradiation time (t) ~ 5 seconds with different laser power densities (*i.e.*, irradiation doses) modulated using a step variable neutral density (ND) filter. It should be noted here that no rastering of the laser was performed in this



Figure 4.2: Schematic of the laser irradiation setup.

study. DI water provides the necessary oxidizing environment for the photo-oxidation reaction. [2, 6, 136] Due to its higher refractive index in comparison to air, DI water also allows for a higher numerical aperture (NA) objective lens (spot size = 540 nm), which localizes the effects of photo-oxidation, thus making it easier to analyze the entire affected area within the field of view of the TEM. It should be noted that use of the dichroic mirror in the setup is required for image capture by the camera and reduces the laser power reaching the sample. As a result, laser irradiation dose calculations were performed using power values measured at the sample stage using a power meter.

In our experiments, the laser irradiation dose (D) was varied from $\sim 10^2$ to 10^5 W/cm², which is lower than the dose required for laser-induced thermal ablation of TMDs (MoS₂). [19] Multiple membranes (n \geq 3) were irradiated for each dose. Immediately after irradiation, samples were annealed at 250°C for 90 minutes in a

 Ar/H_2 environment to reduce hydrocarbon contamination during SEM, STEM, and PL analysis. Based on HAADF STEM images and previous reports of annealed nanopores and nanoporous membranes, [34, 168] annealing at these temperatures, well below the decomposition temperatures of TMDs (~ 600-700°C), [107] does not change the size of defects.



Figure 4.3: SEM images of monolayer WS₂ flakes suspended over a holey carbon grid showing photo-oxidation induced damage of suspended membranes before and after laser irradiation with different doses. Scale bars are 2 μ m.

A comparison of SEM images of the samples obtained before and after irradiation revealed varying degrees of photo-degradation of the membranes dependent on laser dose (Figure 4.3) and served as a quick check before further spectroscopic and AC-STEM analysis were performed. Control experiments in air did not show the formation or expansion of defects in membranes upon laser irradiation, regardless of the presence of initial defects, even for irradiation times, t > 4 minutes and doses, $D \sim 10^5 \text{ W/cm}^2$, strongly suggesting the need of a conducive oxidizing environment and illumination condition for defect expansion at the given dose. [34, 136]

4.2.3 PL Study of Defects



Figure 4.4: (a) PL spectra of a pristine suspended monolayer WS₂ membrane before laser irradiation showing three spectral components: neutral exciton, X_0 , trion, X_T , and defect, X_D . (b) PL spectra of suspended WS₂ membranes after exposure (green) at different irradiation doses, each showing the corresponding spectra before the experiment (black). (c) PL peak shift and intensity ratio change before and after irradiation as a function of irradiation dose. (d) Spectral weight percentage in the post-experiment PL spectra as a function of irradiation dose.

To study the effect of laser-induced damage on suspended membranes, we characterize changes in the electronic and physical structure of WS₂ using a combination of PL spectroscopy and AC-STEM imaging, respectively. Figure 4.4a shows the PL spectrum of a pristine suspended monolayer WS₂ membrane. An excitation wavelength of 532 nm (spot size = 940 nm) and incident laser power of ~ 50 μ W were used to prevent unwanted laser-induced degradation during measurements. [19] A strong PL signal is obtained near the direct bandgap value of WS₂ (~ 2.05 eV), which verifies the monolayer quality of our flake. [64] The spectrum is curve-fitted to three Lorentzian components - namely the neutral exciton (X₀), the trion (X_T) and the defect-related (X_D) peaks, which are centered around ~ 2.02, 1.99 and 1.88 eV, respectively. [24, 34] The average spectral weight percentages of the X₀, X_T and X_D peaks were calculated from multiple pristine samples and found to be ~ 74%, 25% and 1%, respectively.

Figure 4.4b shows the normalized PL spectra of the WS₂ membranes before and after laser irradiation at different doses. The before spectra were taken on pristine WS₂ membranes in air prior to immersion and laser irradiation in DI water. The spectra indicated as after were also obtained in air, but after the experiment was completed, *i.e.*, the membranes were immersed in DI water and exposed to laser irradiation. For the non-laser irradiated case (P = 0 W/cm²), samples were immersed in DI water but not exposed to any laser light. The PL peak shift and intensity changes before and after irradiation are plotted for several irradiation doses in Figure 4.4c. The spectral weight percentages of post-irradiation spectra were also calculated and are plotted in Figure 4.4d.

It was observed that the PL peak redshifts for all irradiation doses and the shift increases with increasing dose, while the PL intensity decays with higher laser irradiation doses. The PL shift was calculated at different laser doses averaged over > 5samples for each dose. Specifically, the PL redshift was found to be 5.6 ± 5.0 meV and 5.6 ± 3.6 meV for P = 0 W/cm² and P = 4.80 x 10³ W/cm², respectively, which are both smaller than the PL shift for P = 6.33 x 10⁴ W/cm² (10.6 ± 6.2 meV). We note that the non-zero PL redshift for $P = 0 \text{ W/cm}^2$ is likely due to the formation of a small number of defects due to water exposure under ambient light, which we verify later using AC-STEM analysis (Figure 4.5a). Similar averaged PL shifts for P = 0 W/cm^2 and P = $4.80 \times 10^3 \text{ W/cm}^2$ means that PL shifts are not sensitive to the difference in the density of defects in non-irradiated samples after water exposure and samples irradiated at low doses (< 10^4 W/cm^2) (Figures 4.5a-b). Furthermore, the relatively large error bars in the PL shift also imply that the variation in the density of defects at low doses across different samples is large enough such that the averaged PL shifts are indistinguishable between zero-dose and low-dose (< 10^4 W/cm^2) irradiated samples. As the irradiation dose increases (P = $6.33 \times 10^4 \text{ W/cm}^2$), the defect density increases as expected, leading to a larger PL redshift.

For doses from 0 (pristine) to 10^4 W/cm^2 , the X_T contribution increases while the X₀ peak contribution diminishes. While both peaks decay with increasing laser irradiation dose, a conversion from neutral to charged exciton emission (*i.e.*, n-type doping) is also seen via a redshift and broadening of the PL spectra. We note that this is opposite to what was observed in plasma-irradiated WS₂ in which the X_T contribution decreased. [24] The X_D contribution remains negligible (< 10%) for all laser doses, suggesting a different kind of defect formation compared to electron beam-induced or plasma-induced defects. [24, 34] For higher doses (D ~ 10^5 W/cm^2), the majority of the membranes were seen to break (Figures 4.3 and 4.5d) and the PL spectra obtained after irradiation are extremely weak compared to those obtained before irradiation (> 800-fold decay). The direct dependence of laser-induced effects on the laser power we observe (decay of X₀ and X_T) is similar to what has been observed for WSe_2 [2] but contrary to the power independence in the case of MoS_2 . [136]

Defects, substrate effects and chemical doping are known to induce n-type doping of TMDs. [113, 186, 192] We can rule out any substrate effects for our case as we are analyzing only suspended membranes. Since membranes are annealed after laser irradiation, we also preclude any doping due to O_2/H_2O adsorption. [112, 128] While we do observe oxide formation on our flakes due to DI water exposure (from our AC-STEM analysis as shown in Figures 4.5 and 4.7a), we do not see a net PL blueshift or X₀ peak contribution enhancement expected from oxide-induced p-type doping, shown previously by several studies. [117, 189, 208] Defect-induced doping is also known to reduce exciton lifetime in TMDs which can in turn decrease the PL intensity. [185] This suggests that while laser-induced defects degrade the membrane, they also introduce defect-induced n-type doping, which is the dominant doping mechanism, in the membrane. It should be noted that the relatively large error bars (~ 60-70%) for dose = 6.33×10^4 W/cm² in Figure 4.4c-d indicate a wider distribution in defect sizes and large defect density in the regime of higher irradiation doses, which we confirm later using AC-STEM analysis (Figure 4.7).

4.2.4 AC-STEM Study of Defects

Bulk properties of laser-irradiated TMD flakes have been studied previously using spectroscopy, optical microscopy and atomic force microscopy. [2, 6, 53, 93, 136] While monolayer TMDs are known to be more resistant to laser degradation than their few-layer counterparts, the former was still seen to undergo decay, which was attributed



Figure 4.5: (Top row) Low-magnification HAADF AC-STEM images of suspended nanoporous WS₂ membranes after exposure to laser irradiation doses of (a) 0, (b) 4.80×10^3 , (c) 6.33×10^4 , and (d) 6.31×10^5 W/cm² with (bottom row) highmagnification images of selected defects. The defect shown for 0 W/cm² (green) represents a defect that formed due to photo-oxidation under ambient conditions. The low-magnification image shown for 6.31×10^5 W/cm² (row (d), top) is one of the few membranes that did not become structurally weakened and (row (d), bottom) one which collapsed at this dose.

to the presence of intrinsic lattice defects in the monolayer basal plane. [2, 136] Indeed, the introduction of defects in the form of nanopores in suspended monolayers and subsequent laser irradiation was demonstrated to expand the nanopore at a controllable rate as a function of laser dose. [34] However, to our knowledge, the effects of laser irradiation on intact monolayers and the fabrication of laser-induced defects have not yet been explored at the atomic level. A better understanding of the laser-induced defect creation would allow for not only better control of the process
for scalable applications but also the manipulation of the properties of TMDs.

To observe the effects of laser irradiation on our WS_2 membranes, we characterize the exposed samples using AC-STEM, which enables structural observations of micron-scale membranes as well as atomic-scale damage. Representative membranes for laser irradiation doses of 0, 4.80×10^3 , 6.33×10^4 , and $6.31 \times 10^5 \text{ W/cm}^2$ are shown in Figure 4.5a-d, with corresponding AC-STEM images of a single defect outlined in yellow shown underneath. We note that the term defect is taken here to mean any region of the membrane which does not contain an intact WS_2 lattice. All the membranes shown were part of the same carbon grid and, as a result, were subjected to the same pre- and post-processing procedures. Regardless of laser irradiation dose, all flakes demonstrate the formation of white islands visible in the TEM images not present initially, which, as discussed later, were determined to be tungsten oxide (WO_3) through EELS analysis (Figure 4.7a). Most of the pristine $(D = 0 \text{ W/cm}^2)$ samples are intact with a few photo-induced triangular defects over a suspended area of ~ 5 μ m². This suggests that tungsten oxide islands and a small number of defects form even during water exposure under ambient light. With increasing laser irradiation dose, the observed defects have larger areas with a noticeably higher density. At the highest dose (D $\sim 10^5$ W/cm²), the defected area is large enough such that the membrane is structurally weakened and therefore collapses. Two such membranes irradiated at 6.31×10^5 W/cm², one of which did not collapse, are shown in Figure 4.5d.

In order to better understand both the composition and structure of individual defects in the nanoporous membranes, we obtain atomic resolution AC-STEM images.



Figure 4.6: (a-b) AC-STEM image of typical photo-oxidation induced defects showing a number of features - (i) defect area (outlined in yellow in a), (ii) nanopore(s) inside the defect, (iii) amorphous carbon-filled part of the defect, (iv) tungsten-oxide-filled part of the defect, and (v) tungsten oxide island in the vicinity of the defect. (c) AC-STEM image of a defect that is fully clogged by amorphous carbon and oxide and (d) a closer view of the edge of the defect showing an intact WS_2 lattice and amorphous nature of the oxide.

Figure 4.6a shows the morphology of a typical laser-induced defect (D ~ 10^3 W/cm²), outlined in yellow. EELS analysis of the bright islands visible on the irradiated membrane reveals a peak at an energy loss of 532 eV that corresponds to the oxygen K-edge (Figure 4.7a). This peak is only observed in the bright clustered features and not elsewhere on the membrane. The oxide is also seen to deposit irregularly inside the expanded defect, held together by an amorphous, carbon-based matrix. Closer observation of defect edges shows the clear demarcation of the intact WS₂ lattice and the amorphous carbon inside the defect, while no clear lattice structure is seen in the oxide (Figure 4.6c-d). We note that unlike molybdenum-based TMDs, where the absence of molybdenum oxide (MoO₃) after photo-oxidation experiments was attributed to dissolution of the oxide in water, [19, 136] previous reports on tungstenbased TMDs using X-ray photoelectron spectroscopy and scanning photoemission



Figure 4.7: (a) EELS spectra of the suspended region (orange) and oxide region (blue) from Figure 4.6a, exhibiting the oxygen K-edge only in the oxide region. The carbon peak is from hydrocarbon contamination. (b) Effective nanopore diameter distribution and (c) percentage of the total nanoporous region as a function of laser irradiation dose.

microscopy have indicated the appearance of tungsten oxide oxidation states after laser exposure. [2, 6, 106, 111] This agrees with our direct observations of oxide islands on the laser-irradiated WS₂ membranes. The amorphous carbon, which is seen to clog part of the defects, shows up in the EELS background spectrum (Figure 4.7a) and is likely the result of the polymer-based transfer process and/or the underlying perforated carbon film. [98, 118, 124, 142] Under prolonged electron beam (AC-STEM) exposure, the carbon contamination is seen to expand until it ultimately clogs the defect entirely. Although the carbon contamination decreases the total nanoporous area of the membrane, it also reduces the minimum effective hole size to the nanometer scale and gives strength to the suspended membranes, which can facilitate catalysis applications.

We classify regions of the laser-induced defects into two distinct parts: an amorphous carbon-clogged region and a nanoporous region (Figure 4.6a). For very large defects (Figure 4.6b), multiple disjointed nanopores are present due to interspersed oxide clusters held together by the amorphous carbon, thus giving a perforated appearance to a single defect (Figure 4.6b). We quantify the dimensions of the nanopores in the suspended membranes using a thresholding function in ImageJ and obtain a distribution of the effective nanopore diameter as a function of laser irradiation dose (Figure 4.7b). Effective nanopore diameter is taken here to be the diameter of a single circular nanopore with the same area as the irregularly-shaped nanopore inside the defect. The smallest defect observed in our samples has an area of $\sim 300 \text{ nm}^2$ while the minimum effective nanopore diameter was found to be $\sim 15 \text{ nm}$. With increasing laser irradiation dose, an increase in both the average and maximum effective nanopore diameter is seen. Calculating the nanoporous area percentage of the exposed membranes results in a linear dependence on the laser irradiation dose given by the empirical formula:

Nanoporous area (%) =
$$a * D + b$$
 (4.1)

where $a = 1.2 \times 10^{-4} \text{ cm}^2/\text{W}$ and b = 0.42 are the fitting parameters (Figure 4.7c).

From our observations, the photo-oxidation mechanism seems to occur in two ways: (i) formation of oxide islands via reaction of water or dissolved oxygen with the WS₂ lattice and possible replacement or dislocation of sulfur atoms, [6] and (ii) oxidation and expansion of intrinsic defects into triangular defect clusters via reaction of dissolved oxygen with the dangling bonds of the defects. [34, 136] The oxide that is formed by the latter process clogs the defect held together by amorphous carbon that is present from the transfer process. If the expanded defect becomes large enough (> 300 nm²), the carbon-clogged region collapses and gives rise to nanopores inside the defect. It should be noted here that based on previous studies using higher laser powers the observed defects are not expected to be thermally-induced as the maximum power reaching the membrane was measured and limited to below 2 mW (P ~ 1.44 mW) during our irradiation experiments. [2, 125, 167]

4.2.5 Conclusion

In this section, we demonstrated the fabrication of atomically-thin WS_2 membranes with tunable porosity via a photo-oxidation-induced process that avoids many of the sensitive processing conditions required of other techniques. While no laser-induced defects were seen in air, an aqueous environment produced defects for laser irradiation doses in the range 10^2 - 10^5 W/cm². We found that the creation of defects leads to the relative lowering of the concentration of neutral excitons compared to trions (*i.e.*, n-type doping), combined with a decrease in PL peak intensity with increase in irradiation dose due to defect-related degradation. AC-STEM images of the irradiated membranes show triangular clustered defects, which contain a combination of nanopores and tungsten oxide islands held together by an amorphous carbon matrix, which arises due to the PMMA-based sample preparation. The smallest defect size obtained was $\sim 300 \text{ nm}^2$, while the minimum effective diameter of nanopores inside the defect was ~ 15 nm. Tunable membrane porosity was also realized through a linear dependence of nanoporous area percentage on the laser irradiation dose, with mechanical collapse of most of the membranes at doses $\sim 10^5 \text{ W/cm}^2$. Combined with computer-controlled, time-resolved laser rastering in a desired pattern (not used in this study), these observations lay the foundation for facile and scalable fabrication

of TMD nanopores and nanoporous membranes.

4.3 Ion Transport Through MoS₂ Nanoporous Membranes

The results presented here were published in the article "Angstrom-Size Defect Creation and Ionic Transport through Pores in Single-Layer MoS₂" by Thiruraman, J.P., Fujisawa, K., Danda, G., Das, P.M., Zhang, T., Bolotsky, A., Perea-López, N., Nicolaï, A., Senet, P., Terrones, M. and Drndić, M., Nano letters, 18(3), pp. 1651-1659 (2018).

4.3.1 Background

Ionic and molecular transport through individual solid-state nanopores has been studied thanks to the ability to fabricate nanometer scale holes in thin membranes. [16] In contrast, ionic transport through smaller, sub-nanometer pores and nanoporous two-dimensional (2D) membranes has not yet been explored in detail, although these systems present fascinating opportunities to study phenomena at the atomic scale. Most studies infer the conductance and sub-nanometer pore diameters indirectly from modeling. [69, 147] With the recent availability of 2D materials [101] that can be suspended as membranes [124] and the ability to image atomic-scale defects, [135] it is now possible to study the fundamental principles behind ion flow through subnanometer pores. [69] A few recent papers have reported transport measurements in individual molybdenum disulfide (MoS_2) sub-nanometer pores. [46, 48]

Thin nanoporous membranes containing a large number of pores provide opportunities for fluid filtration, molecular analysis, and energy generation. In waterdesalination applications, there is a demand for high-throughput, where atomic-scale pores (atomic vacancies in the material) provide unique benefits. This is because (i) water transport scales inversely with membrane thickness allowing for high water fluxes and (ii) membranes with sub-nanometer pores are highly selective. [26, 29, 165, 178] Previous experiments explored ionic transport in nanoporous graphene membranes. [133, 134, 178] Heiranian *et al.* indicated the benefits of MoS_2 pores compared to graphene. [66] To the best of our knowledge, there have been no studies of transport in nanoporous MoS_2 membranes.

In this section, ionic transport measurements through MoS_2 membranes with a population of sub-nanometer pores introduced by controlled Ga^+ ion irradiation at 30 kV are reported. We study the vacancy defects and the resulting properties of the suspended MoS_2 lattices using AC-STEM, Raman spectroscopy, and photoluminescence (PL) spectroscopy. We observe the longitudinal acoustic (LA) band and defect-related PL and determine the vacancy-defect size distribution as a function of Ga^+ ion irradiation dose, showing the median defect diameter in the range of 0.3-0.4 nm.

4.3.2 Ion-Induced Defect Fabrication

Single-layer MoS_2 triangular-flakes were synthesized via a halide-assisted powder vaporization method (Figure 4.8a) by our collaborators at Pennsylvania State University. [96] The presence of single-layer material was confirmed by fluorescence microscopy (Figure 4.8b, 673 nm bandpass filtered). While single-layer MoS_2 shows strong photoluminescence, the signal is quenched in multilayered MoS_2 . [161] Similar



Figure 4.8: (a) Optical image and (b) fluorescence image (673 nm centered bandpass filtered) of as-grown single-layer MoS_2 . (c) Schematic illustration of focused Ga⁺ ion beam based irradiation process. (d) Raman and (e) photoluminescence (PL) spectra of the pristine and the Ga⁺ ion irradiated MoS_2 .

to graphene, [68] polycrystalline MoS₂ fractures at grain boundaries under strain. [35] To maintain the rigidness of the material, single crystal MoS₂ was focused on. Single-layer MoS₂ flakes were transferred onto carbon grids [99] or SiN_x [124] using a polymethyl methacrylate-assisted transfer. Atomic vacancy-defects were introduced by rastering the Ga⁺ ion probe over a certain area (Figure 4.8c) using a focused ion beam (FIB). [18, 122] The degree of defectiveness was controlled by varying the Ga⁺ ion dose from 6.25 x 10^{12} ions/cm² until the PL signal of the irradiated MoS₂ fell into noise level (2.50 x 10^{13} ions/cm²). After prolonged irradiation, the fluorescence signal was suppressed regardless of dose.

The effect of Ga^+ ion irradiation on MoS_2 flakes was investigated by Raman spectroscopy and PL spectroscopy (panels d and e of Figure 4.8, respectively). After Ga^+ ion irradiation of the MoS_2 , several Raman peaks located around 200 cm⁻¹, in the vicinity of the longitudinal acoustic (LA) band emerged, whereas the first-order in-plane (E') and out-of-plane (A₁') modes remained unaffected. [122] The LA band consists of several peaks including LA (~ M), LA (~ K), and a van Hove singularity at the saddle point between the K- and M-points in the Brillouin zone. [18] Because these LA (~ M) and LA (~ K) modes far from the Γ -point are only activated when defects are introduced into the MoS₂ lattice, their relative intensity with respect to the A₁' mode (I(LA)/I(A₁')) can be used as an indicator of the degree of crystallinity. [18, 122] The relative intensity, I(LA)/I(A₁') increased with higher Ga⁺ ion doses (see the inset of Figure 4.8d), as expected.

The PL of the MoS₂ flakes was found to be sensitive to ion irradiation. [169] For pristine MoS₂, there were two peaks at 1.88 and 2.03 eV in the PL spectra, corresponding to the A and B exciton peaks. The A exciton peak was composed of two subpeaks with energy at 1.88 eV (neutral exciton: A₀) and 1.82 eV (trion: A⁻). [113] After Ga⁺ ion irradiation, the neutral exciton A₀ was suppressed and a new peak, a bound exciton (D) located at ~ 1.72 eV, emerged. This newly emerged photoemission peak can be correlated to defect-mediated radiative recombination processes. [17, 24, 169] The bound exciton peak is also observed when the MoS₂ is irradiated by α -particles [169] and energetic plasma. [24] The spectral weight of the bound exciton peak becomes higher with increasing Ga⁺ ion dose, similar to the relative intensity of the LA band, and at a dose of 2.5 x 10¹³ ions/cm², the PL intensity becomes close to the noise level. The enhancement of the LA band and the suppression of the neutral exciton reflect a qualitative increase of defectiveness (e.g., number and size of vacancies), within MoS₂ monocrystals after the Ga⁺ ion irradiation. However, upon the collision between an ion and an atom, several different types of defects including topological defects, atomic vacancies, holes, and amorphous regions can form [101] depending on the ion species and their kinetic energy. [58] A quantitative study of vacancy-defects; such as type, density and edge termination of defects, is required but cannot be completed using only the techniques above. In this context, Surwade *et al.* mentioned that even when similar optical signatures were observed in differently prepared defective graphene membrane, the water-transport properties of the membranes varied. [165]

In 2D systems, the type of vacancy-defects introduced by ion irradiation changes depending on the ion characteristics and kinetic energy. [91, 195] For the electron irradiation of MoS₂ using a parallel beam, monosulfur vacancies (V_S) and disulfur vacancies (V_{2S}) are predominant. [58, 135] With increased electron irradiation time, sulfur vacancies migrate and aggregate into line defects. [80] In contrast to electrons, the mass of an ion is larger and varies, resulting in ion-species-dependent effects. Molecular dynamics (MD) simulations suggest that higher mass causes more displacement and sputtering of atoms. [91, 195] Direct observation of vacancy-defects created by Ga⁺ ion irradiation is needed to fully understand their characteristics.

Ion-irradiated MoS₂ membranes were investigated by aberration-corrected scanning transmission election microscopy (AC-STEM). Figure 4.9a shows high-angle annular dark-field (HAADF) images of MoS₂ before and after Ga⁺ ion irradiation for different doses: 0 (pristine), $6.25 \ge 10^{12}$, $8.16 \ge 10^{12}$, $1.11 \ge 10^{13}$, $1.60 \ge 10^{13}$, and $2.50 \ge 10^{13}$ ions/cm². HAADF intensity changes depending on $\sim Z^2$ (Z: atomic number), allowing us to roughly distinguish elements (Mo or S) and, therefore, the atomic con-



Figure 4.9: (a) AC-STEM image of the pristine and the Ga^+ ion irradiated MoS_2 with different ion doses. (b) High-magnification AC-STEM image of atomic vacancies with different atomic configuration. These images were used to perform the statistical analysis of defects shown in Figure 4.10 and are described in the text.

figuration of vacancy-defects. Figure 4.9b shows magnified STEM-HAADF images of several atomic vacancies. Metal atomic vacancies with several sulfur vacancies (V_{xMo+yS}) are formed rather than sulfur vacancies (V_S) , topological defects (bond changing), or amorphous regions. This is consistent with expected sputtering behavior due to the relatively higher mass of Ga⁺ in comparison to electrons and leads to disulfur or monosulfur termination-rich edge structures.

To investigate the effect of the Ga⁺ ion dose on pore (*i.e.*, vacancy-defect) area and density, statistical analysis was performed on AC-STEM images, as shown in Figure 4.10. Within the irradiation dose ranges used, the pore density increases with larger doses, whereas the pore area remains roughly constant. For the lowest dose (6.25 x 10^{12} ions/cm²), the majority of the atomic pores were single-molybdenum-based vacancies (V_{1Mo+yS}), while the number of missing sulfur atoms varied. With increas-



Figure 4.10: (a) Nanopore density, (b) nanopore area and (c) total pore area percentage were calculated from binary images created from AC-STEM image. (d) Distribution of nanopore diameter for defects produced by Ga⁺ ion irradiation, for different Ga⁺ ion doses. The red (blue)-colored box corresponds to diameter ranges for V_{1Mo+yS} (V_{2Mo+yS}) nanopores which is calculated from simulated STEM-HAADF images by QSTEM (inset, scale bar is 500 pm).

ing Ga⁺ ion dose, the number of double-molybdenum-based vacancies (V_{2Mo+yS}) increased, and some triple-molybdenum-based vacancies were also found (V_{3Mo+yS}; Figure 4.9b), exhibiting low-intensity STEM-HAADF signals inside the defect. Because these defects were observed far from carbon contamination caused by the transfer process and the STEM-HAADF intensity was close to V_S, the structure inside the defect was assigned to sulfur. When the Ga⁺ ion dose reached 2.50 x 10¹³ ion/cm², the density of pores with size >0.8 nm in diameter increased (Figure 4.10).

4.3.3 Nanoporous Device Characterization



Figure 4.11: (a) Experimental setup to measure the conductance of nanoporous MoS_2 membranes. (b) Current-voltage plot of a MoS_2 device irradiated with a dose of 1.60 x 10¹³ ions/cm² showing a nonlinear trend in the voltage range of $V_B = \pm$ 0.8 V (orange, device P). (bottom inset) Current-voltage curves for a pristine MoS_2 membrane (black) and the same irradiated MoS_2 device for $V_B = \pm$ 0.1 V. (top inset) STEM image of a suspended MoS_2 membrane exposed to a Ga⁺ ion dose of 2.50 x 10¹³ ions/cm².

To observe the ionic transport characteristics of the Ångström-size defects in the MoS_2 membranes, we implement the device setup shown in Figure 4.11a. A MoS_2 flake was selected under an optical microscope and then transferred over a SiN_x window with a ~ 200 nm diameter FIB hole. [34, 121] The membrane was then irradiated with doses ranging from 6.25×10^{12} to 2.50×10^{13} ions/cm² to create atomic vacancies with average single defect diameters between 0.4 and 0.5 nm. The top inset of Figure 4.11b shows a STEM image of a suspended MoS_2 membrane over a FIB hole exposed with a dose of 2.50×10^{13} ions/cm². A resultant nonlinear current-voltage (I-V) curve is shown in Figure 4.11b for an irradiated MoS_2 membrane (device P, dose of 1.60 x 10^{13} ions/cm²). For comparison, a similar trace is shown in the bottom inset for a pristine sample demonstrating a baseline ionic conductance (G = dI/dV) of ~ 10 pS.



Figure 4.12: (a) Current vs time traces at an applied voltage of $V_B = 0.1$ V and (b) the corresponding power spectral density for two devices (device P and Q, dose of $1.60 \times 10^{13} \text{ ions/cm}^2$). (c) Current vs time trace for device Q at an applied voltage of $V_B = 1$ V showing an increase in conductance in steps, suggesting membrane damage. (inset) Noise at an initial conductance of 20 nS before the high-voltage induced damage (zeroth point) is obtained from panel b.

Figure 4.12 show ionic current traces at $V_B = 0.1$ V and the corresponding current noise for two devices (dose of 1.60 x 10^{13} ions/cm²). It should be noted that only those devices are shown here that have an ionic conductance of G > 5 nS in the range of ± 0.1 V. For devices exhibiting G < 5 nS, the defects are too small to allow significant ionic flow below a certain threshold voltage (discussed below), thus making ionic noise extraction difficult. The power spectral density was extracted from the current traces and fit to the following equation:

$$PSD = (I^2 A)/f^{\alpha} \tag{4.2}$$

where PSD is the power spectral density, I is the corresponding ionic current, f is the frequency, A is the noise coefficient, and α is the low-frequency noise exponent. All of the devices showed a noise exponent value of $\alpha \approx 1$ and noise coefficient of $A \approx 10^{-4} \cdot 10^{-5}$, suggesting dominant low-frequency noise as has been demonstrated previously in 2D nanopore devices. [103, 121, 209]

To further investigate the stability of our devices, we applied a constant $V_B = 1$ V and monitored the change in ionic current for another device with the same dose (device Q, dose = 1.60 x 10¹³ ions/cm²), as shown in Figure 4.12c. The current increased in jumps from 20 nA (from Figure Figure 4.12a) to 250 nA, suggesting incremental damage of the membrane as opposed to gradual increase of defect sizes. [49] The noise coefficients extracted from each section and plotted in the inset (zeroth point is from Figure Figure 4.12a) reveal that the low-frequency noise decreases with increasing conductance, in accordance with a power law:

$$A = 0.48G^{-2} \tag{4.3}$$

A similar trend of increasing conductance was also observed in other devices when V_B exceeded ± 0.8 V. To ensure that we did not damage our devices during ionic experiments, V_B was kept in the range of ± 0.5 V for most of our devices.



Figure 4.13: (a) Ionic current vs voltage (I-V) curves measured for pristine and irradiated MoS_2 membranes with dose 1 (6.25 x 10^{12} ions/cm²), dose 2 (1.11 x 10^{13} ions/cm²), and dose 3 (2.5 x 10^{13} ions/cm²). The applied sweep rate was between 5 and 20 mV per second. (b) Corresponding dI/dV with respect to voltage for nonlinear I-V curves in panel a.

4.3.4 Ionic Transport Through Sub-nm Defects

Figure 4.13a presents the I-V curves for a pristine membrane and 15 devices irradiated at three different doses (dose $1 = 6.25 \ge 10^{12}$, dose $2 = 1.11 \ge 10^{13}$, and dose $3 = 2.50 \ge 10^{13}$ ions/cm²). We note that while a total of 25 devices were irradiated and tested, 10 of these yielded negligible ionic conductance (G $\approx 10 \text{ pS}$) comparable to non-irradiated, *i.e.*, pristine samples, close to our detection limit, and are not shown here. In Figure 4.13a, several of the 15 I-V curves plotted overlap (6 red, dose 1; 4 green, dose 2; 5 blue, dose 3; 1 black, pristine). A total of six representative differential conductances (dI/dV) for doses 1-3 are shown in Figure 4.13b. Collective current passing through multiple Ångström-size pores in a MoS₂ membrane resulting in nonlinear I-V curves at voltages $V_B \ge 0.1$ V are displayed by ~ 80% of the devices. At lower voltages ($V_B < 0.1 \text{ V}$), the I-V curves are linear (Figure 4.13a inset). Such nonlinear trends have been observed previously for sub-nanometer 2D pores and were attributed to stripping of the ionic solvation shell at higher driving voltages. [48, 69] About 20% of devices showed higher conductance (G > 5 nS) and a linear trend, even up to 1 V. This may be due to the merging of individual Ångström-size pores or their enlargement over time, resulting in higher conductance values and linear I-V curve behavior that is typically observed in nanometer-size pores that are well-described by the continuum model. [48]

Using the previously stated AC-STEM analysis (Figure 4.10), we estimate the number of pores, N, and their diameters, D, within the nanoporous membranes for the various doses. The mean and maximum diameters of pores are 0.4 and 0.8 nm for dose 1, 0.5 and 0.9 nm for dose 2, and 0.5 and 1.3 nm for dose 3, respectively. The number of pores ranges from N \approx 300 for dose 1, N \approx 700 for dose 2, and N \approx 1200 for dose 3. This is estimated using the results from Figure 4.10a and calculating how many pores of average diameter are contained in the suspended area $\sim 3 \times 10^4$ nm². From the defect size distributions, we also estimate the number of pores with diameters larger than the hydrated K⁺ ion diameter (the smaller ion compared to Cl⁻), [115] where D > 0.6 nm: ~ 30 , ~ 120 and ~ 240 for doses 1-3, respectively. Similarly, the estimated number of pores with D ≥ 1 nm are zero for doses 1 and 2 and ~ 34 for dose 3. Doses 1-3 were chosen because they produce well-separated, Ångström-size defects. For higher doses, defects start to merge resulting in larger, irregularly shaped pores.

Despite a large number of defects, most of them are very small, below \sim 5 Å.



Figure 4.14: Conductance G is shown as a function of the pore diameter for both the continuum (black, yellow, orange, and pink) and molecular dynamics (MD) simulated (blue) models. Plotted are also G values from the MD model discussed in the text for five pores shown in Figure 4.15, the experimentally obtained G values for MoS_2 nanoporous membranes and single nanopores, and reported values from previous works on SiN, [175] a-Si, [146, 155] and MoS_2 nanopores. [46, 48]

Based on molecular dynamics simulations, [66] such pores are expected to be too small for ions to flow through but should allow water molecules to pass. We therefore expect the measured conductance in the range of $V_B = \pm 0.1$ V of the irradiated MoS₂ membranes to be low, and indeed, it was found to be ~ 1 nS in 80% of the devices shown in Figure 4.13a. The average conductances of the irradiated devices were ~ 1 nS for doses 1 and 2, increasing to ~ 10 nS for dose 3. We compare and contrast the irradiated membranes to single nanopore devices in Figure 4.14, which plots the conductances of the nanoporous membranes as a function of the effective defect diameter (including the mean G for each dose), as well as the conductances of two single MoS₂ nanopore devices that were drilled using AC-STEM with effective D values of ~ 1.4 and ~ 1.1 nm (shown in Figure 4.15(i),(ii)). Effective D is defined as D of a circle with the same area as the pore (calculated using ImageJ software). We also compare our results with previously published literature on single pores (less than 2 nm in diameter) in MoS_2 , [46, 48] thinned silicon nitride, [175] and amorphous silicon membranes with D ≈ 0.3 to 2 nm. [146, 155]

The average conductance measured for dose 1 is ~ 1.4 nS, slightly higher than that of dose 2 (1.11 x 10^{13} ions/cm²), where the measured average conductance is 0.9 nS. While the larger dose 2 is expected to give larger mean conductance than dose 1, the averaged experimental results can be explained by the following two factors: (i) the mean vacancy sizes obtained from these two doses are very close to each other, *i.e.*, 0.4 and 0.5 nm for dose 1 and dose 2, respectively, as shown in Figure 4.10; and (ii) the spread in the conductance values for different samples, irradiated at each dose, is larger than the difference between the averages of the two doses. Dose 3 (2.5 x 10^{13} ions/cm²), which is the highest dose used, yielded the largest mean conductance (~ 10 nS), consistent with expectations that samples irradiated with larger doses yield higher ionic conductance.

We observe variation of 2 orders of magnitude in the experimental conductance values corresponding to single pores and nanoporous membranes, from $G \approx 0.1$ to 10 nS for single pores with $D \approx 0.3$ to 2 nm, and $G \approx 1$ to 100 nS for nanoporous devices with an average D of ≈ 0.5 nm. This enhancement in conductance is expected due to the presence of multiple nanopores. However, the scatter among devices could come from several reasons, including the variations in atomic structure and edge terminations that can result in different properties of the pores when they are introduced in the salt solutions. This has not yet been explored experimentally. It is also challenging to determine the diameter accurately. The effective D used on the x-axis is measured from AC-TEM images with pores in vacuum before ionic measurements, and it can change later (for example, due to expansion or contamination in solution). [34]

4.3.5 MD Simulation of Sub-nm Defects

Figure 4.15: AC-STEM images of individual MoS₂ pores: (i) pore 1 and (ii) pore 2 with effective diameters of ~ 1.4 and 1.1 nm, respectively. Corresponding allatom structures used in non-equilibrium molecular dynamics (NEMD) simulations are presented aside. Mo, S₂, and S atoms are shown in blue, yellow, and purple spheres, respectively. (iii) Atomic structure of an equivalent circular pore of diameter of ~ 0.9 nm. QSTEM simulations [78] for vacancy-defects caused by (iv) 1Mo and 1S (V_{1Mo+1S}) missing and (v) 3Mo and 5S atoms (V_{5Mo+3S}).

To estimate the conductance of the pores with precise and stable diameters, molecular dynamics simulations were performed by our collaborators at Laboratoire Interdisciplinaire Carnot de Bourgogne. [140] Figure 4.15i-v shows the five configurations that were tested, where pores 1 and 2 (the same as in Figure 4.16b) correspond to AC-

STEM drilled MoS₂ pores with effective diameters of ~ 1.4 and 1.1 nm, respectively (see Figure S9), and pore 3 corresponds to a perfectly circular pore of effective diameter 0.9 nm, and finally, V_{1Mo+1S} and V_{3Mo+5S} , which represent the defect vacancies with one of the smallest and largest diameters, respectively (Figure 4.10). The conductances of these five pores are plotted in Figure 4.14. As shown in Figure 4.16a, I-V curves were computed for each system via MD simulations, and conductances G were obtained by the linear fitting of I-V curves with 0.15 V < V_B < 0.6 V. Figure 4.16b presents the conductance obtained for all the simulated pores, showing a variation of 3 orders of magnitude depending on the pore size. Pores 1 and 2 are characterized by conductance values of 3.3 and 3.5 nS, respectively, which agree within a factor of 2-3 with the experimental values (~ 10 and 1.5 nS in Figure 4.14), while pore 3 shows a conductance of 0.4 nS. The conductance G drops drastically for pore 3 because of its smaller diameter in comparison with pore 1 and 2 and because its diameter is close to the limiting diameter value for zero conductance. Finally, pores made of defects V_{1Mo+1S} (D ≈ 0.4 nm) and V_{3Mo+5S} (D ≈ 0.6 nm) exhibited a negligible conductance of G \approx 0.02-0.03 nS, confirming the fact that pores made of defects smaller than \sim 0.6 nm do not conduct ions in our experiments.

In this size range (< 1 nm), small changes in D by ~ 0.1 nm result in conductance changes by 1 order of magnitude or more (notice the sharp drop of the blue line in Figure 4.14). Using the MD simulations, an empirical linear model of open conductance for MoS₂ pores less than 3 nm was obtained and plotted as the blue line in Figure 4.14:



Figure 4.16: (a) I-V characteristics and (b) conductance G panel computed from NEMD simulations for the five pores shown in Figure 4.15. Error bars represent the standard deviation from the ionic current computed from NEMD runs.

$$G_{MD} = C(D - D_{min}) \tag{4.4}$$

where G_{MD} is the pore conductance derived from MD, C = 8.92 S/m is the conductivity of KCl ions through single-layer MoS₂ nanopores less than 3 nm, and $D_{min} = 0.73$ nm is the minimum pore diameter for ionic flow. Furthermore, in Figure 4.14, this model derived from MD simulations [140] is featured as a blue line along with the black, yellow, pink, and orange fit lines G (L and D), which represent the continuum model for the conductance for different values of pore thickness, L.

Ionic measurements have validated the continuum model for pores with nanometerscale diameters and shown that an effective pore thickness, $L \approx 1.6$ nm is a good approximation for MoS₂. [103] This corresponds to the black line in Figure 4.14. Here, the pore is modeled as a system of three resistors in series. The interior of the nanopore is modeled as a cylindrical resistor,

$$R_p = \frac{1}{\sigma} \frac{4L}{\pi D^2} \tag{4.5}$$

where σ is the conductivity of the electrolyte, L is the thickness of the nanopore, and D is its diameter. Additionally, there is an access resistance in series on each side where current paths converge from the bulk electrolyte into the pore, [67]

$$R_a = \frac{1}{\sigma} \frac{1}{2D} \tag{4.6}$$

The total resistance of the single nanopore, R_1 , is given by the sum of the three resistances, the interior of the nanopore and two access resistances:

$$R_1 = R_p + 2R_a = \frac{1}{\sigma} \left(\frac{4L}{\pi D^2} + \frac{1}{D} \right)$$
(4.7)

This gives us an equation for conductance through a single nanopore of diameter D and thickness L:

$$G_1 = \frac{\sigma \pi D^2}{4L + \pi D} \tag{4.8}$$

We stress that G (L = 1.6 nm, D) does not fit the conductance measured in single MoS_2 sub-nanometer pores plotted in Figure 4.14, in contrast to the agreement found in pores with larger diameters (D > 1 nm). In fact, the data clearly show that small pores conduct less than expected from this model, and a better fit can be obtained by assuming a larger pore thickness (the pink line in Figure 4.14 where L = 13 nm) or by assuming an effectively smaller diameter. The orange line, G (L = 1.6 nm,

D - 0.6 nm) corresponds to a continuum model, assuming that the pore diameter is smaller than the actual diameter by 0.6 nm, meaning that a pore with D = 0.6 nm would give zero current. This best fit is also consistent with the assumption that for a KCl ionic solution, K⁺ is the smallest hydrated ion with a diameter of 0.6 nm, such that a pore diameter, D = 0.6 nm, will effectively resist the transport of ions. [69, 115] This model closely resembles the linear model of conductance obtained from MD simulations for pores smaller than 2 nm. For large D, G (L = 1.6 nm, D = 0.6 nm) \approx G (L = 1.6 nm, D), and the two models converge (orange and black lines). To our knowledge, besides these data points, the only comparable pores that have been measured in the diameter range of less than 2 nm are Si/SiO₂ pores [175] and ultrathin Si₃N₄. [49, 103] The corresponding fit G (L = 3 nm, D) is shown in yellow for comparison to G \approx 3 to 10 nS for D \approx 0.8 to 2 nm.

4.3.6 Conclusion

In summary, we demonstrated the creation of nanoporous MoS_2 membranes containing ~ 100-1000 Ångström-size pores with a mean diameter of ~ 0.5 nm using Ga⁺ ion irradiation, and characterization of the devices by atomic-resolution imaging and Raman and PL spectroscopy. The measured conductance in 80% of the devices was of the order of 1 nS. We also fabricated two single ~ 1 nm diameter MoS_2 pores with corresponding AC-STEM images, and G was found to be ~ 1 and 10 nS. Our experiments and comparison with single-pore data demonstrate that conductance must occur only through the few larger pores within the distribution and that the majority of the defects do not allow ions to pass through. These results have a direct application for water desalination. Our MD simulations reveal that the defects with diameters less than ~ 0.6 nm are too small for ions to go through and result in negligible conductance < 20 pS. This conductance is comparable to the conductance obtained in a controlled experiment using a pristine membrane. Future studies may use atomic-resolution imaging to correlate the ionic transport measurements with the detailed information on the atomic structure of the individual conducting defects. Furthermore, there is a need for the modeling of nanoporous membranes containing a large distribution of Ångström-size pores that can now be fulfilled using the AC-STEM insights provided by this work.

4.4 Summary

In this chapter, we fabricated TMD nanoporous membranes and characterized the fabrication techniques and ion selectivity of MoS_2 membranes. In intact suspended $WS2_2$ membranes, we induced defects using laser irradiation, observed as a decay of PL signal, and a relative increase in the trion contribution compared to that of the neutral exciton, suggesting defect-related n-type doping and degradation of the membrane. AC-STEM images show the nucleation of tungsten oxide islands on the membrane, and the formation of triangular defect clusters containing a combination of nanopores and oxide-filled regions, providing insight at the atomic level into the photo-oxidation process in TMDs. A linear dependence of the nanoporous area percentage on the laser irradiation dose over the range of 10^2-10^5 W/cm² is observed. We also fabricated sub-nanometer vacancies in suspended MoS_2 via Ga⁺ ion irradiation,

producing membranes containing ~ 300 to 1200 pores with average and maximum diameters of ~ 0.5 and ~ 1 nm, respectively. Ionic current versus voltage was observed to be nonlinear and conductance is comparable to that of ~ 1 nm diameter single MoS₂ pores, proving that the smaller pores in the distribution display negligible conductance. Consistently, MD simulations showed that pores with diameters < 0.6 nm are almost impermeable to ionic flow.

Bibliography

- Aghigh, A., Alizadeh, V., Wong, H. Y., Islam, M. S., Amin, N., and Zaman, M. (2015). Recent advances in utilization of graphene for filtration and desalination of water: a review. *Desalination*, 365:389–397.
- [2] Ahn, S., Kim, G., Nayak, P. K., Yoon, S. I., Lim, H., Shin, H.-J., and Shin, H. S. (2016). Prevention of transition metal dichalcogenide photodegradation by encapsulation with h-BN layers. ACS nano, 10(9):8973–8979.
- [3] Ai, Y., Liu, J., Zhang, B., and Qian, S. (2010). Field effect regulation of DNA translocation through a nanopore. *Analytical chemistry*, 82(19):8217–8225.
- [4] Akinwande, D., Petrone, N., and Hone, J. (2014). Two-dimensional flexible nanoelectronics. *Nature communications*, 5:5678.
- [5] Ambrosi, A., Sofer, Z., and Pumera, M. (2015). 2H → 1T phase transition and hydrogen evolution activity of MoS₂, MoSe₂, WS₂ and WSe₂ strongly depends on the MX₂ composition. *Chemical Communications*, 51(40):8450–8453.
- [6] Atkin, P., Lau, D., Zhang, Q., Zheng, C., Berean, K., Field, M., Ou, J., Cole, I.,

Daeneke, T., and Kalantar-Zadeh, K. (2017). Laser exposure induced alteration of WS_2 monolayers in the presence of ambient moisture. 2D Materials, 5(1):015013.

- [7] Bae, S., Kim, H., Lee, Y., Xu, X., Park, J.-S., Zheng, Y., Balakrishnan, J., Lei, T., Kim, H. R., Song, Y. I., et al. (2010). Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nature nanotechnology*, 5(8):574.
- [8] Balan, A., Chien, C.-C., Engelke, R., and Drndić, M. (2015). Suspended solidstate membranes on glass chips with sub 1-pF capacitance for biomolecule sensing applications. *Scientific reports*, 5:17775.
- [9] Banerjee, S., Shim, J., Rivera, J., Jin, X., Estrada, D., Solovyeva, V., You, X., Pak, J., Pop, E., Aluru, N., et al. (2012). Electrochemistry at the edge of a single graphene layer in a nanopore. ACS nano, 7(1):834–843.
- [10] Banerjee, S., Wilson, J., Shim, J., Shankla, M., Corbin, E. A., Aksimentiev, A., and Bashir, R. (2015). Slowing DNA transport using graphene–DNA interactions. *Advanced functional materials*, 25(6):936–946.
- [11] Beal, A. and Liang, W. (1976). Excitons in 2H-WSe₂ and 3R-WS₂. Journal of Physics C: Solid State Physics, 9(12):2459.
- [12] Belkin, M., Maffeo, C., Wells, D. B., and Aksimentiev, A. (2013). Stretching and controlled motion of single-stranded DNA in locally heated solid-state nanopores. ACS nano, 7(8):6816–6824.
- [13] 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_2 using Raman spectroscopy. *Scientific reports*, 3:1755.

- Bertolazzi, S., Brivio, J., and Kis, A. (2011). Stretching and breaking of ultrathin MoS₂. ACS nano, 5(12):9703–9709.
- [15] Blake, P., Brimicombe, P. D., Nair, R. R., Booth, T. J., Jiang, D., Schedin, F., Ponomarenko, L. A., Morozov, S. V., Gleeson, H. F., Hill, E. W., et al. (2008). Graphene-based liquid crystal device. *Nano letters*, 8(6):1704–1708.
- [16] Branton, D., Deamer, D. W., Marziali, A., Bayley, H., Benner, S. A., Butler, T., Di Ventra, M., Garaj, S., Hibbs, A., Huang, X., et al. (2008). The potential and challenges of nanopore sequencing. *Nature biotechnology*, 26(10):1146.
- [17] Carozo, V., Wang, Y., Fujisawa, K., Carvalho, B. R., McCreary, A., Feng, S., Lin, Z., Zhou, C., Perea-López, N., Elías, A. L., et al. (2017). Optical identification of sulfur vacancies: Bound excitons at the edges of monolayer tungsten disulfide. *Science advances*, 3(4):e1602813.
- [18] Carvalho, B. R., Wang, Y., Mignuzzi, S., Roy, D., Terrones, M., Fantini, C., Crespi, V. H., Malard, L. M., and Pimenta, M. A. (2017). Intervalley scattering by acoustic phonons in two-dimensional MoS₂ revealed by double-resonance Raman spectroscopy. *Nature communications*, 8:14670.
- [19] Castellanos-Gomez, A., Barkelid, M., Goossens, A., Calado, V. E., van der Zant,
 H. S., and Steele, G. A. (2012). Laser-thinning of MoS₂: on demand generation of a single-layer semiconductor. *Nano letters*, 12(6):3187–3192.

- [20] Chang, H.-Y., Yang, S., Lee, J., Tao, L., Hwang, W.-S., Jena, D., Lu, N., and Akinwande, D. (2013). High-performance, highly bendable MoS₂ transistors with high-k dielectrics for flexible low-power systems. ACS nano, 7(6):5446–5452.
- [21] Cheng, L., Huang, W., Gong, Q., Liu, C., Liu, Z., Li, Y., and Dai, H. (2014). Ultrathin WS₂ nanoflakes as a high-performance electrocatalyst for the hydrogen evolution reaction. Angewandte Chemie International Edition, 53(30):7860–7863.
- [22] Cherf, G. M., Lieberman, K. R., Rashid, H., Lam, C. E., Karplus, K., and Akeson, M. (2012). Automated forward and reverse ratcheting of DNA in a nanopore at 5-å precision. *Nature biotechnology*, 30(4):344.
- [23] Chernikov, A., Berkelbach, T. C., Hill, H. M., Rigosi, A., Li, Y., Aslan, O. B., Reichman, D. R., Hybertsen, M. S., and Heinz, T. F. (2014). Exciton binding energy and nonhydrogenic Rydberg series in monolayer WS₂. *Physical review letters*, 113(7):076802.
- [24] Chow, P. K., Jacobs-Gedrim, R. B., Gao, J., Lu, T.-M., Yu, B., Terrones, H., and Koratkar, N. (2015). Defect-induced photoluminescence in monolayer semiconducting transition metal dichalcogenides. ACS nano, 9(2):1520–1527.
- [25] Clarke, J., Wu, H.-C., Jayasinghe, L., Patel, A., Reid, S., and Bayley, H. (2009). Continuous base identification for single-molecule nanopore DNA sequencing. *Nature nanotechnology*, 4(4):265.
- [26] Cohen-Tanugi, D. and Grossman, J. C. (2012). Water desalination across nanoporous graphene. *Nano letters*, 12(7):3602–3608.

- [27] Cohen-Tanugi, D. and Grossman, J. C. (2014a). Mechanical strength of nanoporous graphene as a desalination membrane. *Nano letters*, 14(11):6171–6178.
- [28] Cohen-Tanugi, D. and Grossman, J. C. (2014b). Water permeability of nanoporous graphene at realistic pressures for reverse osmosis desalination. *The Journal of chemical physics*, 141(7):074704.
- [29] Cohen-Tanugi, D., McGovern, R. K., Dave, S. H., Lienhard, J. H., and Grossman, J. C. (2014). Quantifying the potential of ultra-permeable membranes for water desalination. *Energy & Environmental Science*, 7(3):1134–1141.
- [30] Conley, H. J., Wang, B., Ziegler, J. I., Haglund Jr, R. F., Pantelides, S. T., and Bolotin, K. I. (2013). Bandgap engineering of strained monolayer and bilayer MoS₂. Nano letters, 13(8):3626–3630.
- [31] Cook, J. B., Kim, H.-S., Yan, Y., Ko, J. S., Robbennolt, S., Dunn, B., and Tolbert, S. H. (2016). Mesoporous MoS₂ as a transition metal dichalcogenide exhibiting pseudocapacitive Li and Na-ion charge storage. *Advanced Energy Materials*, 6(9).
- [32] Coulter, W. H. (1953). Means for counting particles suspended in a fluid. US Patent 2,656,508.
- [33] Danda, G., Das, P. M., and Drndić, M. (2018). Laser-induced fabrication of nanoporous monolayer WS₂ membranes. 2D Materials.
- [34] Danda, G., Masih Das, P., Chou, Y.-C., Mlack, J. T., Parkin, W. M., Naylor,
 C. H., Fujisawa, K., Zhang, T., Fulton, L. B., Terrones, M., Johnson, A. T. C.,

and Drndić, M. (2017). Monolayer WS_2 nanopores for DNA translocation with light-adjustable sizes. ACS nano, 11(2):1937–1945.

- [35] Dang, K. Q. and Spearot, D. E. (2014). Effect of point and grain boundary defects on the mechanical behavior of monolayer MoS₂ under tension via atomistic simulations. *Journal of Applied Physics*, 116(1):013508.
- [36] Das, S., Chen, H.-Y., Penumatcha, A. V., and Appenzeller, J. (2012). High performance multilayer MoS₂ transistors with scandium contacts. *Nano letters*, 13(1):100–105.
- [37] de la Rosa, C. J. L., Sun, J., Lindvall, N., Cole, M. T., Nam, Y., Löffler, M., Olsson, E., Teo, K. B., and Yurgens, A. (2013). Frame assisted H₂O electrolysis induced H₂ bubbling transfer of large area graphene grown by chemical vapor deposition on Cu. *Applied Physics Letters*, 102(2):022101.
- [38] de Zoysa, R. S. S., Jayawardhana, D. A., Zhao, Q., Wang, D., Armstrong, D. W., and Guan, X. (2009). Slowing DNA translocation through nanopores using a solution containing organic salts. *The Journal of Physical Chemistry B*, 113(40):13332– 13336.
- [39] Deamer, D. W. and Akeson, M. (2000). Nanopores and nucleic acids: prospects for ultrarapid sequencing. *Trends in biotechnology*, 18(4):147–151.
- [40] Dekker, C. (2007). Solid-state nanopores. *Nature nanotechnology*, 2(4):209.
- [41] Derrington, I. M., Butler, T. Z., Collins, M. D., Manrao, E., Pavlenok, M.,

Niederweis, M., and Gundlach, J. H. (2010). Nanopore DNA sequencing with MspA. *Proceedings of the National Academy of Sciences*, 107(37):16060–16065.

- [42] Di Fiori, N., Squires, A., Bar, D., Gilboa, T., Moustakas, T. D., and Meller, A. (2013). Optoelectronic control of surface charge and translocation dynamics in solid-state nanopores. *Nature nanotechnology*, 8(12):946.
- [43] Dolinska, J., Chidambaram, A., Adamkiewicz, W., Estili, M., Lisowski, W., Iwan, M., Palys, B., Sudholter, E. J., Marken, F., Opallo, M., et al. (2016). Synthesis and characterization of porous carbon–MoS₂ nanohybrid materials: electrocatalytic performance towards selected biomolecules. *Journal of Materials Chemistry B*, 4(8):1448–1457.
- [44] Du, X., Skachko, I., Barker, A., and Andrei, E. Y. (2008). Approaching ballistic transport in suspended graphene. *Nature nanotechnology*, 3(8):491.
- [45] Ellis, J. K., Lucero, M. J., and Scuseria, G. E. (2011). The indirect to direct band gap transition in multilayered MoS₂ as predicted by screened hybrid density functional theory. *Applied Physics Letters*, 99(26):261908.
- [46] Feng, J., Graf, M., Liu, K., Ovchinnikov, D., Dumcenco, D., Heiranian, M., Nandigana, V., Aluru, N. R., Kis, A., and Radenovic, A. (2016a). Single-layer MoS₂ nanopores as nanopower generators. *Nature*, 536(7615):197.
- [47] Feng, J., Liu, K., Bulushev, R. D., Khlybov, S., Dumcenco, D., Kis, A., and Radenovic, A. (2015a). Identification of single nucleotides in MoS₂ nanopores. *Nature nanotechnology*, 10(12):1070.

- [48] Feng, J., Liu, K., Graf, M., Dumcenco, D., Kis, A., Di Ventra, M., and Radenovic, A. (2016b). Observation of ionic Coulomb blockade in nanopores. *Nature materials*, 15(8):850.
- [49] Feng, J., Liu, K., Graf, M., Lihter, M., Bulushev, R. D., Dumcenco, D., Alexander, D. T., Krasnozhon, D., Vuletic, T., Kis, A., et al. (2015b). Electrochemical reaction in single layer MoS₂: nanopores opened atom by atom. *Nano letters*, 15(5):3431–3438.
- [50] Fischbein, M. D. and Drndić, M. (2008). Electron beam nanosculpting of suspended graphene sheets. Applied physics letters, 93(11):113107.
- [51] Fologea, D., Uplinger, J., Thomas, B., McNabb, D. S., and Li, J. (2005). Slowing DNA translocation in a solid-state nanopore. *Nano letters*, 5(9):1734–1737.
- [52] Fox, D. S., Zhou, Y., Maguire, P., O'Neill, A., O'Coileáin, C., Gatensby, R., Glushenkov, A. M., Tao, T., Duesberg, G. S., Shvets, I. V., et al. (2015). Nanopatterning and electrical tuning of MoS₂ layers with a subnanometer helium ion beam. *Nano letters*, 15(8):5307–5313.
- [53] Gao, J., Li, B., Tan, J., Chow, P., Lu, T.-M., and Koratkar, N. (2016). Aging of transition metal dichalcogenide monolayers. ACS nano, 10(2):2628–2635.
- [54] Gao, L., Ren, W., Xu, H., Jin, L., Wang, Z., Ma, T., Ma, L.-P., Zhang, Z., Fu, Q., Peng, L.-M., et al. (2012). Repeated growth and bubbling transfer of graphene with millimetre-size single-crystal grains using platinum. *Nature communications*, 3:699.

- [55] Garaj, S., Hubbard, W., Reina, A., Kong, J., Branton, D., and Golovchenko,
 J. (2010). Graphene as a subnanometre trans-electrode membrane. *Nature*, 467(7312):190.
- [56] Garaj, S., Liu, S., Golovchenko, J. A., and Branton, D. (2013). Moleculehugging graphene nanopores. Proceedings of the National Academy of Sciences, 110(30):12192–12196.
- [57] Ghaderi, N. and Peressi, M. (2010). First-principle study of hydroxyl functional groups on pristine, defected graphene, and graphene epoxide. *The Journal of Physical Chemistry C*, 114(49):21625–21630.
- [58] Ghorbani-Asl, M., Kretschmer, S., Spearot, D. E., and Krasheninnikov, A. V. (2017). Two-dimensional MoS₂ under ion irradiation: from controlled defect production to electronic structure engineering. 2D Materials, 4(2):025078.
- [59] Gomez De Arco, L., Zhang, Y., Schlenker, C. W., Ryu, K., Thompson, M. E., and Zhou, C. (2010). Continuous, highly flexible, and transparent graphene films by chemical vapor deposition for organic photovoltaics. ACS nano, 4(5):2865–2873.
- [60] Gourmelon, E., Lignier, O., Hadouda, H., Couturier, G., Bernede, J., Tedd, J., Pouzet, J., and Salardenne, J. (1997). MS₂ (M= W, Mo) photosensitive thin films for solar cells. *Solar Energy Materials and Solar Cells*, 46(2):115–121.
- [61] Gracheva, M. E. and Leburton, J.-P. (2008). Simulation of electrically tunable semiconductor nanopores for ion current/single bio-molecule manipulation. *Journal* of Computational Electronics, 7(1):6–9.
- [62] Graf, D., Molitor, F., Ensslin, K., Stampfer, C., Jungen, A., Hierold, C., and Wirtz, L. (2007). Spatially resolved raman spectroscopy of single-and few-layer graphene. *Nano letters*, 7(2):238–242.
- [63] Gravelle, S., Joly, L., Detcheverry, F., Ybert, C., Cottin-Bizonne, C., and Bocquet, L. (2013). Optimizing water permeability through the hourglass shape of aquaporins. *Proceedings of the National Academy of Sciences*, 110(41):16367– 16372.
- [64] Gutiérrez, H. R., Perea-López, N., Elías, A. L., Berkdemir, A., Wang, B., Lv, R., López-Urías, F., Crespi, V. H., Terrones, H., and Terrones, M. (2012). Extraordinary room-temperature photoluminescence in triangular WS₂ monolayers. *Nano letters*, 13(8):3447–3454.
- [65] He, Y., Tsutsui, M., Fan, C., Taniguchi, M., and Kawai, T. (2011). Controlling DNA translocation through gate modulation of nanopore wall surface charges. ACS nano, 5(7):5509–5518.
- [66] Heiranian, M., Farimani, A. B., and Aluru, N. R. (2015). Water desalination with a single-layer MoS₂ nanopore. *Nature communications*, 6:8616.
- [67] Hille, B. (1968). Pharmacological modifications of the sodium channels of frog nerve. The Journal of general physiology, 51(2):199–219.
- [68] Huang, P. Y., Ruiz-Vargas, C. S., van der Zande, A. M., Whitney, W. S., Levendorf, M. P., Kevek, J. W., Garg, S., Alden, J. S., Hustedt, C. J., Zhu, Y., et al.

(2011). Grains and grain boundaries in single-layer graphene atomic patchwork quilts. *Nature*, 469(7330):389.

- [69] Jain, T., Rasera, B. C., Guerrero, R. J. S., Boutilier, M. S., O'hern, S. C., Idrobo, J.-C., and Karnik, R. (2015). Heterogeneous sub-continuum ionic transport in statistically isolated graphene nanopores. *Nature nanotechnology*, 10(12):1053.
- [70] Jo, S., Ubrig, N., Berger, H., Kuzmenko, A. B., and Morpurgo, A. F. (2014).
 Mono-and bilayer WS₂ light-emitting transistors. *Nano letters*, 14(4):2019–2025.
- [71] Kakavelakis, G., Del Rio Castillo, A. E., Pellegrini, V., Ansaldo, A., Tzourmpakis, P., Brescia, R., Prato, M., Stratakis, E., Kymakis, E., and Bonaccorso, F. (2017). Size-tuning of WSe₂ flakes for high efficiency inverted organic solar cells. *ACS nano*, 11(4):3517–3531.
- [72] Kasianowicz, J. J., Brandin, E., Branton, D., and Deamer, D. W. (1996). Characterization of individual polynucleotide molecules using a membrane channel. *Pro*ceedings of the National Academy of Sciences, 93(24):13770–13773.
- [73] Keyser, U. F., Koeleman, B. N., Van Dorp, S., Krapf, D., Smeets, R. M., Lemay,
 S. G., Dekker, N. H., and Dekker, C. (2006). Direct force measurements on DNA in a solid-state nanopore. *Nature Physics*, 2(7):473.
- [74] Kim, K. S., Zhao, Y., Jang, H., Lee, S. Y., Kim, J. M., Kim, K. S., Ahn, J.-H., Kim, P., Choi, J.-Y., and Hong, B. H. (2009). Large-scale pattern growth of graphene films for stretchable transparent electrodes. *nature*, 457(7230):706.

- [75] Kim, M. S., Yun, S. J., Lee, Y., Seo, C., Han, G. H., Kim, K. K., Lee, Y. H., and Kim, J. (2016). Biexciton emission from edges and grain boundaries of triangular WS₂ monolayers. ACS nano, 10(2):2399–2405.
- [76] Kim, S. J., Choi, K., Lee, B., Kim, Y., and Hong, B. H. (2015). Materials for flexible, stretchable electronics: graphene and 2d materials. *Annual Review of Materials Research*, 45:63–84.
- [77] Kobayashi, T., Bando, M., Kimura, N., Shimizu, K., Kadono, K., Umezu, N., Miyahara, K., Hayazaki, S., Nagai, S., Mizuguchi, Y., et al. (2013). Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll chemical vapor deposition and transfer process. *Applied Physics Letters*, 102(2):023112.
- [78] Koch, C. T. (2002). Determination of core structure periodicity and point defect density along dislocations. PhD thesis, Arizona State University.
- [79] Koenig, S. P., Wang, L., Pellegrino, J., and Bunch, J. S. (2012). Selective molecular sieving through porous graphene. *Nature nanotechnology*, 7(11):728.
- [80] Komsa, H.-P., Kurasch, S., Lehtinen, O., Kaiser, U., and Krasheninnikov, A. V. (2013). From point to extended defects in two-dimensional MoS₂: evolution of atomic structure under electron irradiation. *Physical Review B*, 88(3):035301.
- [81] Kotakoski, J., Santos-Cottin, D., and Krasheninnikov, A. V. (2011). Stability of graphene edges under electron beam: equilibrium energetics versus dynamic effects. ACS nano, 6(1):671–676.

- [82] Kowalczyk, S. W., Grosberg, A. Y., Rabin, Y., and Dekker, C. (2011). Modeling the conductance and DNA blockade of solid-state nanopores. *Nanotechnology*, 22(31):315101.
- [83] Kowalczyk, S. W., Wells, D. B., Aksimentiev, A., and Dekker, C. (2012). Slowing down DNA translocation through a nanopore in lithium chloride. *Nano letters*, 12(2):1038–1044.
- [84] Krishnakumar, P., Gyarfas, B., Song, W., Sen, S., Zhang, P., Krstic, P., and Lindsay, S. (2013). Slowing DNA translocation through a nanopore using a functionalized electrode. ACS nano, 7(11):10319–10326.
- [85] Kuan, A. T., Lu, B., Xie, P., Szalay, T., and Golovchenko, J. A. (2015). Electrical pulse fabrication of graphene nanopores in electrolyte solution. *Applied physics letters*, 106(20):203109.
- [86] Kwok, H., Briggs, K., and Tabard-Cossa, V. (2014). Nanopore fabrication by controlled dielectric breakdown. *PloS one*, 9(3):e92880.
- [87] Kwok, K. M., Ong, S. W. D., Chen, L., and Zeng, H. C. (2017). Constrained growth of MoS₂ nanosheets within a mesoporous silica shell and its effects on defect sites and catalyst stability for H₂S decomposition. ACS Catalysis, 8(1):714–724.
- [88] Larkin, J., Henley, R., Bell, D. C., Cohen-Karni, T., Rosenstein, J. K., and Wanunu, M. (2013). Slow DNA transport through nanopores in hafnium oxide membranes. Acs Nano, 7(11):10121–10128.

- [89] Late, D. J., Huang, Y.-K., Liu, B., Acharya, J., Shirodkar, S. N., Luo, J., Yan, A., Charles, D., Waghmare, U. V., Dravid, V. P., et al. (2013). Sensing behavior of atomically thin-layered MoS₂ transistors. Acs Nano, 7(6):4879–4891.
- [90] Lee, C., Wei, X., Kysar, J. W., and Hone, J. (2008). Measurement of the elastic properties and intrinsic strength of monolayer graphene. *science*, 321(5887):385– 388.
- [91] Lehtinen, O., Kotakoski, J., Krasheninnikov, A., Tolvanen, A., Nordlund, K., and Keinonen, J. (2010). Effects of ion bombardment on a two-dimensional target: atomistic simulations of graphene irradiation. *Physical review B*, 81(15):153401.
- [92] Lehtinen, O., Tsai, I.-L., Jalil, R., Nair, R. R., Keinonen, J., Kaiser, U., and Grigorieva, I. V. (2014). Non-invasive transmission electron microscopy of vacancy defects in graphene produced by ion irradiation. *Nanoscale*, 6(12):6569–6576.
- [93] Li, H., Lu, G., Wang, Y., Yin, Z., Cong, C., He, Q., Wang, L., Ding, F., Yu, T., and Zhang, H. (2013). Mechanical exfoliation and characterization of single-and few-layer nanosheets of WSe₂, TaS₂, and TaSe₂. *Small*, 9(11):1974–1981.
- [94] Li, J., Stein, D., McMullan, C., Branton, D., Aziz, M. J., and Golovchenko, J. A. (2001). Ion-beam sculpting at nanometre length scales. *Nature*, 412(6843):166.
- [95] Li, N., Chai, Y., Dong, B., Liu, B., Guo, H., and Liu, C. (2012). Preparation of porous MoS₂ via a sol–gel route using (NH₄)₂Mo₃S₁₃ as precursor. *Materials Letters*, 88:112–115.

- [96] Li, S., Wang, S., Tang, D.-M., Zhao, W., Xu, H., Chu, L., Bando, Y., Golberg, D., and Eda, G. (2015). Halide-assisted atmospheric pressure growth of large WSe₂ and WS₂ monolayer crystals. *Applied Materials Today*, 1(1):60–66.
- [97] Li, X., Cai, W., An, J., Kim, S., Nah, J., Yang, D., Piner, R., Velamakanni, A., Jung, I., Tutuc, E., et al. (2009). Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science*, 324(5932):1312–1314.
- [98] Lin, Y.-C., Lu, C.-C., Yeh, C.-H., Jin, C., Suenaga, K., and Chiu, P.-W. (2011). Graphene annealing: how clean can it be? *Nano letters*, 12(1):414–419.
- [99] Lin, Y.-C., Zhang, W., Huang, J.-K., Liu, K.-K., Lee, Y.-H., Liang, C.-T., Chu, C.-W., and Li, L.-J. (2012). Wafer-scale MoS₂ thin layers prepared by MoO₃ sulfurization. *Nanoscale*, 4(20):6637–6641.
- [100] Lin, Y.-M., Dimitrakopoulos, C., Jenkins, K. A., Farmer, D. B., Chiu, H.-Y., Grill, A., and Avouris, P. (2010). 100-GHz transistors from wafer-scale epitaxial graphene. *Science*, 327(5966):662–662.
- [101] Lin, Z., Carvalho, B. R., Kahn, E., Lv, R., Rao, R., Terrones, H., Pimenta, M. A., and Terrones, M. (2016). Defect engineering of two-dimensional transition metal dichalcogenides. 2D Materials, 3(2):022002.
- [102] Liu, C., Yu, Z., Neff, D., Zhamu, A., and Jang, B. Z. (2010). Graphene-based supercapacitor with an ultrahigh energy density. *Nano letters*, 10(12):4863–4868.
- [103] Liu, K., Feng, J., Kis, A., and Radenovic, A. (2014a). Atomically thin molyb-

denum disulfide nanopores with high sensitivity for DNA translocation. ACS nano, 8(3):2504–2511.

- [104] Liu, K., Yan, Q., Chen, M., Fan, W., Sun, Y., Suh, J., Fu, D., Lee, S., Zhou, J., Tongay, S., et al. (2014b). Elastic properties of chemical-vapor-deposited monolayer MoS₂, WS₂, and their bilayer heterostructures. *Nano letters*, 14(9):5097–5103.
- [105] Liu, S., Lu, B., Zhao, Q., Li, J., Gao, T., Chen, Y., Zhang, Y., Liu, Z., Fan, Z., Yang, F., et al. (2013). Boron nitride nanopores: highly sensitive dna singlemolecule detectors. *Advanced Materials*, 25(33):4549–4554.
- [106] Lu, J., Lu, J. H., Liu, H., Liu, B., Chan, K. X., Lin, J., Chen, W., Loh, K. P., and Sow, C. H. (2014). Improved photoelectrical properties of MoS₂ films after laser micromachining. Acs Nano, 8(6):6334–6343.
- [107] Lu, X., Utama, M. I. B., Zhang, J., Zhao, Y., and Xiong, Q. (2013). Layer-bylayer thinning of MoS₂ by thermal annealing. *Nanoscale*, 5(19):8904–8908.
- [108] Luan, B., Stolovitzky, G., and Martyna, G. (2012). Slowing and controlling the translocation of DNA in a solid-state nanopore. *Nanoscale*, 4(4):1068–1077.
- [109] Lucchese, M. M., Stavale, F., Ferreira, E. M., Vilani, C., Moutinho, M., Capaz, R. B., Achete, C., and Jorio, A. (2010). Quantifying ion-induced defects and raman relaxation length in graphene. *Carbon*, 48(5):1592–1597.
- [110] Luo, W., Wan, J., Ozdemir, B., Bao, W., Chen, Y., Dai, J., Lin, H., Xu, Y., Gu, F., Barone, V., et al. (2015). Potassium ion batteries with graphitic materials. *Nano letters*, 15(11):7671–7677.

- [111] Ma, S., Zeng, L., Tao, L., Tang, C. Y., Yuan, H., Long, H., Cheng, P. K., Chai, Y., Chen, C., Fung, K. H., et al. (2017). Enhanced photocatalytic activity of WS₂ film by laser drilling to produce porous WS₂/WO₃ heterostructure. *Scientific reports*, 7(1):3125.
- [112] Ma, Y., Dai, Y., Guo, M., Niu, C., Lu, J., and Huang, B. (2011). Electronic and magnetic properties of perfect, vacancy-doped, and nonmetal adsorbed MoSe₂, MoTe₂ and WS₂ monolayers. *Physical Chemistry Chemical Physics*, 13(34):15546–15553.
- [113] Mak, K. F., He, K., Lee, C., Lee, G. H., Hone, J., Heinz, T. F., and Shan, J. (2013). Tightly bound trions in monolayer MoS₂. *Nature materials*, 12(3):207.
- [114] Mak, K. F., Lee, C., Hone, J., Shan, J., and Heinz, T. F. (2010). Atomically thin MoS₂: a new direct-gap semiconductor. *Physical review letters*, 105(13):136805.
- [115] Marcus, Y. (1988). Ionic radii in aqueous solutions. *Chemical Reviews*, 88(8):1475–1498.
- [116] Mayorov, A. S., Gorbachev, R. V., Morozov, S. V., Britnell, L., Jalil, R., Ponomarenko, L. A., Blake, P., Novoselov, K. S., Watanabe, K., Taniguchi, T., et al. (2011). Micrometer-scale ballistic transport in encapsulated graphene at room temperature. *Nano letters*, 11(6):2396–2399.
- [117] McDonnell, S., Azcatl, A., Addou, R., Gong, C., Battaglia, C., Chuang, S., Cho, K., Javey, A., and Wallace, R. M. (2014). Hole contacts on transition metal

dichalcogenides: Interface chemistry and band alignments. *ACS nano*, 8(6):6265–6272.

- [118] McGilvery, C. M., Goode, A. E., Shaffer, M. S., and McComb, D. W. (2012). Contamination of holey/lacey carbon films in STEM. *Micron*, 43(2-3):450–455.
- [119] Mehmood, F., Pachter, R., Lu, W., and Boeckl, J. J. (2013). Adsorption and diffusion of oxygen on single-layer graphene with topological defects. *The Journal* of Physical Chemistry C, 117(20):10366–10374.
- [120] Meller, A., Nivon, L., and Branton, D. (2001). Voltage-driven DNA translocations through a nanopore. *Physical Review Letters*, 86(15):3435.
- [121] Merchant, C. A., Healy, K., Wanunu, M., Ray, V., Peterman, N., Bartel, J., Fischbein, M. D., Venta, K., Luo, Z., Johnson, A. C., et al. (2010). DNA translocation through graphene nanopores. *Nano letters*, 10(8):2915–2921.
- [122] Mignuzzi, S., Pollard, A. J., Bonini, N., Brennan, B., Gilmore, I. S., Pimenta, M. A., Richards, D., and Roy, D. (2015). Effect of disorder on Raman scattering of single-layer MoS₂. *Physical Review B*, 91(19):195411.
- [123] Mihovilovic, M., Hagerty, N., and Stein, D. (2013). Statistics of DNA capture by a solid-state nanopore. *Physical Review Letters*, 110(2):028102.
- [124] Mlack, J. T., Das, P. M., Danda, G., Chou, Y.-C., Naylor, C. H., Lin, Z., López,
 N. P., Zhang, T., Terrones, M., Johnson, A. C., et al. (2017). Transfer of monolayer
 TMD WS₂ and Raman study of substrate effects. *Scientific Reports*, 7:43037.

- [125] Najmaei, S., Liu, Z., Ajayan, P., and Lou, J. (2012). Thermal effects on the characteristic Raman spectrum of molybdenum disulfide (MoS₂) of varying thicknesses. *Applied Physics Letters*, 100(1):013106.
- [126] Nakane, J. J., Akeson, M., and Marziali, A. (2003). Nanopore sensors for nucleic acid analysis. *Journal of Physics: Condensed Matter*, 15(32):R1365.
- [127] Nam, S.-W., Rooks, M. J., Kim, K.-B., and Rossnagel, S. M. (2009). Ionic field effect transistors with sub-10 nm multiple nanopores. *Nano letters*, 9(5):2044–2048.
- [128] Nan, H., Wang, Z., Wang, W., Liang, Z., Lu, Y., Chen, Q., He, D., Tan, P., Miao, F., Wang, X., et al. (2014). Strong photoluminescence enhancement of MoS₂ through defect engineering and oxygen bonding. ACS nano, 8(6):5738–5745.
- [129] Niedringhaus, T. P., Milanova, D., Kerby, M. B., Snyder, M. P., and Barron,
 A. E. (2011). Landscape of next-generation sequencing technologies. *Analytical chemistry*, 83(12):4327–4341.
- [130] Novoselov, K. S. and Geim, A. (2007). The rise of graphene. Nat. Mater, 6(3):183–191.
- [131] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., and Firsov, A. A. (2004). Electric field effect in atomically thin carbon films. *science*, 306(5696):666–669.
- [132] O'Hern, S. C., Boutilier, M. S., Idrobo, J.-C., Song, Y., Kong, J., Laoui, T., Atieh, M., and Karnik, R. (2014). Selective ionic transport through tunable sub-

nanometer pores in single-layer graphene membranes. Nano letters, 14(3):1234– 1241.

- [133] O'Hern, S. C., Jang, D., Bose, S., Idrobo, J.-C., Song, Y., Laoui, T., Kong, J., and Karnik, R. (2015). Nanofiltration across defect-sealed nanoporous monolayer graphene. *Nano letters*, 15(5):3254–3260.
- [134] O'Hern, S. C., Stewart, C. A., Boutilier, M. S., Idrobo, J.-C., Bhaviripudi, S., Das, S. K., Kong, J., Laoui, T., Atieh, M., and Karnik, R. (2012). Selective molecular transport through intrinsic defects in a single layer of CVD graphene. *ACS nano*, 6(11):10130–10138.
- [135] Parkin, W. M., Balan, A., Liang, L., Das, P. M., Lamparski, M., Naylor, C. H., Rodríguez-Manzo, J. A., Johnson, A. C., Meunier, V., and Drndić, M. (2016).
 Raman shifts in electron-irradiated monolayer MoS₂. ACS nano, 10(4):4134–4142.
- [136] Parzinger, E., Miller, B., Blaschke, B., Garrido, J. A., Ager, J. W., Holleitner,
 A., and Wurstbauer, U. (2015). Photocatalytic stability of single-and few-layer
 MoS₂. ACS nano, 9(11):11302–11309.
- [137] Peimyoo, N., Shang, J., Cong, C., Shen, X., Wu, X., Yeow, E. K., and Yu, T. (2013). Nonblinking, intense two-dimensional light emitter: monolayer WS₂ triangles. ACS nano, 7(12):10985–10994.
- [138] Pendergast, M. T. M. and Hoek, E. M. (2011). A review of water treatment membrane nanotechnologies. *Energy & Environmental Science*, 4(6):1946–1971.

- [139] Perea-López, N., Elías, A. L., Berkdemir, A., Castro-Beltran, A., Gutiérrez, H. R., Feng, S., Lv, R., Hayashi, T., López-Urías, F., Ghosh, S., et al. (2013). Photosensor device based on few-layered WS₂ films. *Advanced Functional Materials*, 23(44):5511–5517.
- [140] Perez, M. D. B., Senet, P., Meunier, V., and Nicolaï, A. (2017). Computational investigation of the ionic conductance through molybdenum disulfide (MoS₂) nanopores. WSEAS Trans. Circuits Sys.
- [141] Ping, J., Wang, Y., Wu, J., and Ying, Y. (2011). Development of an allsolid-state potassium ion-selective electrode using graphene as the solid-contact transducer. *Electrochemistry Communications*, 13(12):1529–1532.
- [142] Pirkle, A., Chan, J., Venugopal, A., Hinojos, D., Magnuson, C., McDonnell, S., Colombo, L., Vogel, E., Ruoff, R., and Wallace, R. (2011). The effect of chemical residues on the physical and electrical properties of chemical vapor deposited graphene transferred to SiO₂. *Applied Physics Letters*, 99(12):122108.
- [143] Plechinger, G., Nagler, P., Kraus, J., Paradiso, N., Strunk, C., Schüller, C., and Korn, T. (2015). Identification of excitons, trions and biexcitons in singlelayer WS₂. physica status solidi (RRL)-Rapid Research Letters, 9(8):457–461.
- [144] Puster, M., Rodríguez-Manzo, J. A., Balan, A., and Drndić, M. (2013). Toward sensitive graphene nanoribbon–nanopore devices by preventing electron beaminduced damage. ACS nano, 7(12):11283–11289.
- [145] Ramakrishna Matte, H., Gomathi, A., Manna, A. K., Late, D. J., Datta, R.,

Pati, S. K., and Rao, C. (2010). MoS_2 and WS_2 analogues of graphene. Angewandte Chemie International Edition, 49(24):4059–4062.

- [146] Rodríguez-Manzo, J. A., Puster, M., Nicolaï, A., Meunier, V., and Drndić, M. (2015). DNA translocation in nanometer thick silicon nanopores. ACS nano, 9(6):6555–6564.
- [147] Rollings, R. C., Kuan, A. T., and Golovchenko, J. A. (2016). Ion selectivity of graphene nanopores. *Nature communications*, 7:11408.
- [148] Rosenstein, J. K., Wanunu, M., Merchant, C. A., Drndic, M., and Shepard, K. L. (2012). Integrated nanopore sensing platform with sub-microsecond temporal resolution. *Nature methods*, 9(5):487.
- [149] Ross, J. S., Klement, P., Jones, A. M., Ghimire, N. J., Yan, J., Mandrus, D., Taniguchi, T., Watanabe, K., Kitamura, K., Yao, W., et al. (2014). Electrically tunable excitonic light-emitting diodes based on monolayer WSe₂ p-n junctions. *Nature nanotechnology*, 9(4):268.
- [150] Scheuschner, N., Ochedowski, O., Kaulitz, A.-M., Gillen, R., Schleberger, M., and Maultzsch, J. (2014). Photoluminescence of freestanding single-and few-layer MoS₂. *Physical Review B*, 89(12):125406.
- [151] Schneider, G. F. and Dekker, C. (2012). DNA sequencing with nanopores. *Nature biotechnology*, 30(4):326.
- [152] Schneider, G. F., Kowalczyk, S. W., Calado, V. E., Pandraud, G., Zandbergen,

H. W., Vandersypen, L. M., and Dekker, C. (2010). DNA translocation through graphene nanopores. *Nano letters*, 10(8):3163–3167.

- [153] Schoch, R. B., Han, J., and Renaud, P. (2008). Transport phenomena in nanofluidics. *Reviews of modern physics*, 80(3):839.
- [154] Schwierz, F. (2010). Graphene transistors. Nature nanotechnology, 5(7):487.
- [155] Shekar, S., Niedzwiecki, D. J., Chien, C.-C., Ong, P., Fleischer, D. A., Lin, J., Rosenstein, J. K., Drndić, M., and Shepard, K. L. (2016). Measurement of DNA translocation dynamics in a solid-state nanopore at 100 ns temporal resolution. *Nano letters*, 16(7):4483–4489.
- [156] Shi, H., Pan, H., Zhang, Y.-W., and Yakobson, B. I. (2013). Quasiparticle band structures and optical properties of strained monolayer MoS₂ and WS₂. *Physical Review B*, 87(15):155304.
- [157] Singh, E., Kim, K. S., Yeom, G. Y., and Nalwa, H. S. (2017). Atomically thinlayered molybdenum disulfide (MoS₂) for bulk-heterojunction solar cells. ACS applied materials & interfaces, 9(4):3223–3245.
- [158] Sint, K., Wang, B., and Král, P. (2008). Selective ion passage through functionalized graphene nanopores. *Journal of the American Chemical Society*, 130(49):16448–16449.
- [159] Skrabalak, S. E. and Suslick, K. S. (2005). Porous MoS₂ synthesized by ultrasonic spray pyrolysis. *Journal of the American Chemical Society*, 127(28):9990– 9991.

- [160] Smeets, R. M., Keyser, U. F., Krapf, D., Wu, M.-Y., Dekker, N. H., and Dekker, C. (2006). Salt dependence of ion transport and DNA translocation through solidstate nanopores. *Nano letters*, 6(1):89–95.
- [161] Splendiani, A., Sun, L., Zhang, Y., Li, T., Kim, J., Chim, C.-Y., Galli, G., and Wang, F. (2010). Emerging photoluminescence in monolayer MoS₂. Nano letters, 10(4):1271–1275.
- [162] Stephenson, T., Li, Z., Olsen, B., and Mitlin, D. (2014). Lithium ion battery applications of molybdenum disulfide (MoS₂) nanocomposites. *Energy & Environmental Science*, 7(1):209–231.
- [163] Storm, A., Chen, J., Ling, X., Zandbergen, H., and Dekker, C. (2003). Fabrication of solid-state nanopores with single-nanometre precision. *Nature materials*, 2(8):537.
- [164] Su, L., Yu, Y., Cao, L., and Zhang, Y. (2015). Effects of substrate type and material-substrate bonding on high-temperature behavior of monolayer WS₂. Nano Research, 8(8):2686–2697.
- [165] Surwade, S. P., Smirnov, S. N., Vlassiouk, I. V., Unocic, R. R., Veith, G. M., Dai, S., and Mahurin, S. M. (2015). Water desalination using nanoporous singlelayer graphene. *Nature nanotechnology*, 10(5):459–464.
- [166] Tan, H., Fan, Y., Zhou, Y., Chen, Q., Xu, W., and Warner, J. H. (2016). Ultrathin 2D photodetectors utilizing chemical vapor deposition grown WS₂ with graphene electrodes. ACS nano, 10(8):7866–7873.

- [167] Terrones, H., Del Corro, E., Feng, S., Poumirol, J., Rhodes, D., Smirnov, D., Pradhan, N., Lin, Z., Nguyen, M., Elias, A., et al. (2014). New first order Ramanactive modes in few layered transition metal dichalcogenides. *Scientific reports*, 4:4215.
- [168] Thiruraman, J. P., Fujisawa, K., Danda, G., and Masih Das, P. (2018). Angstrom-size defect creation and ionic transport through pores in single-layer MoS₂. Nano letters.
- [169] Tongay, S., Suh, J., Ataca, C., Fan, W., Luce, A., Kang, J. S., Liu, J., Ko, C., Raghunathanan, R., Zhou, J., et al. (2013). Defects activated photoluminescence in two-dimensional semiconductors: interplay between bound, charged, and free excitons. *Scientific reports*, 3:2657.
- [170] Tsai, C., Chan, K., Abild-Pedersen, F., and Nørskov, J. K. (2014a). Active edge sites in MoSe₂ and WSe₂ catalysts for the hydrogen evolution reaction: a density functional study. *Physical Chemistry Chemical Physics*, 16(26):13156–13164.
- [171] Tsai, M.-L., Su, S.-H., Chang, J.-K., Tsai, D.-S., Chen, C.-H., Wu, C.-I., Li, L.-J., Chen, L.-J., and He, J.-H. (2014b). Monolayer MoS₂ heterojunction solar cells. ACS nano, 8(8):8317–8322.
- [172] Van der Bruggen, B., Vandecasteele, C., Van Gestel, T., Doyen, W., and Leysen, R. (2003). A review of pressure-driven membrane processes in wastewater treatment and drinking water production. *Environmental Progress & Sustainable Energy*, 22(1):46–56.

- [173] Venkatesan, B. M. and Bashir, R. (2011). Nanopore sensors for nucleic acid analysis. *Nature nanotechnology*, 6(10):615.
- [174] Venkatesan, B. M., Estrada, D., Banerjee, S., Jin, X., Dorgan, V. E., Bae, M.-H., Aluru, N. R., Pop, E., and Bashir, R. (2011). Stacked graphene-Al₂O₃ nanopore sensors for sensitive detection of DNA and DNA–protein complexes. ACS nano, 6(1):441–450.
- [175] Venta, K., Shemer, G., Puster, M., Rodríguez-Manzo, J. A., Balan, A., Rosenstein, J. K., Shepard, K., and Drndić, M. (2013). Differentiation of short, singlestranded DNA homopolymers in solid-state nanopores. ACS nano, 7(5):4629–4636.
- [176] Venta, K. E., Zanjani, M. B., Ye, X., Danda, G., Murray, C. B., Lukes, J. R., and Drndić, M. (2014). Gold nanorod translocations and charge measurement through solid-state nanopores. *Nano letters*, 14(9):5358–5364.
- [177] Wallace, P. R. (1947). The band theory of graphite. *Physical Review*, 71(9):622.
- [178] Wang, L., Boutilier, M. S., Kidambi, P. R., Jang, D., Hadjiconstantinou, N. G., and Karnik, R. (2017). Fundamental transport mechanisms, fabrication and potential applications of nanoporous atomically thin membranes. *Nature nanotechnology*, 12(6):509.
- [179] Wang, L., Drahushuk, L. W., Cantley, L., Koenig, S. P., Liu, X., Pellegrino, J., Strano, M. S., and Bunch, J. S. (2015a). Molecular valves for controlling gas phase transport made from discrete ångström-sized pores in graphene. *Nature nanotechnology*, 10(9):785.

- [180] Wang, X., Zhi, L., and Müllen, K. (2008). Transparent, conductive graphene electrodes for dye-sensitized solar cells. *Nano letters*, 8(1):323–327.
- [181] Wang, Y., Cong, C., Yang, W., Shang, J., Peimyoo, N., Chen, Y., Kang, J., Wang, J., Huang, W., and Yu, T. (2015b). Strain-induced direct-indirect bandgap transition and phonon modulation in monolayer WS₂. *Nano Research*, 8(8):2562– 2572.
- [182] Wang, Y., Feng, Y., Chen, Y., Mo, F., Qian, G., Yu, D., Wang, Y., and Zhang, X. (2015c). Morphological and structural evolution of WS₂ nanosheets irradiated with an electron beam. *Physical Chemistry Chemical Physics*, 17(4):2678–2685.
- [183] Wanunu, M., Dadosh, T., Ray, V., Jin, J., McReynolds, L., and Drndić, M. (2010). Rapid electronic detection of probe-specific microRNAs using thin nanopore sensors. *Nature nanotechnology*, 5(11):807.
- [184] Wanunu, M. and Meller, A. (2007). Chemically modified solid-state nanopores. Nano letters, 7(6):1580–1585.
- [185] Wu, Z., Luo, Z., Shen, Y., Zhao, W., Wang, W., Nan, H., Guo, X., Sun, L., Wang, X., You, Y., et al. (2016). Defects as a factor limiting carrier mobility in WSe₂: A spectroscopic investigation. *Nano Research*, 9(12):3622–3631.
- [186] Wu, Z., Zhao, W., Jiang, J., Zheng, T., You, Y., Lu, J., and Ni, Z. (2017). Defect activated photoluminescence in WSe₂ monolayer. *The Journal of Physical Chemistry C*, 121(22):12294–12299.

- [187] Xiao, D., Liu, G.-B., Feng, W., Xu, X., and Yao, W. (2012). Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides. *Physical Review Letters*, 108(19):196802.
- [188] Yamada, Y., Murota, K., Fujita, R., Kim, J., Watanabe, A., Nakamura, M., Sato, S., Hata, K., Ercius, P., Ciston, J., et al. (2014). Subnanometer vacancy defects introduced on graphene by oxygen gas. *Journal of the American Chemical Society*, 136(6):2232–2235.
- [189] Yamamoto, M., Dutta, S., Aikawa, S., Nakaharai, S., Wakabayashi, K., Fuhrer, M. S., Ueno, K., and Tsukagoshi, K. (2015). Self-limiting layer-by-layer oxidation of atomically thin WSe₂. *Nano letters*, 15(3):2067–2073.
- [190] Yan, J.-A., Xian, L., and Chou, M. (2009). Structural and electronic properties of oxidized graphene. *Physical review letters*, 103(8):086802.
- [191] Yanagi, I., Akahori, R., Hatano, T., and Takeda, K.-i. (2014). Fabricating nanopores with diameters of sub-1 nm to 3 nm using multilevel pulse-voltage injection. *Scientific reports*, 4:5000.
- [192] Yang, L., Majumdar, K., Liu, H., Du, Y., Wu, H., Hatzistergos, M., Hung, P., Tieckelmann, R., Tsai, W., Hobbs, C., et al. (2014). Chloride molecular doping technique on 2D materials: WS₂ and MoS₂. Nano letters, 14(11):6275–6280.
- [193] Yeh, L.-H., Zhang, M., Joo, S. W., and Qian, S. (2012). Slowing down DNA translocation through a nanopore by lowering fluid temperature. *Electrophoresis*, 33(23):3458–3465.

- [194] Yin, Z., Li, H., Li, H., Jiang, L., Shi, Y., Sun, Y., Lu, G., Zhang, Q., Chen, X., and Zhang, H. (2011). Single-layer MoS₂ phototransistors. ACS nano, 6(1):74–80.
- [195] Yoon, K., Rahnamoun, A., Swett, J. L., Iberi, V., Cullen, D. A., Vlassiouk, I. V., Belianinov, A., Jesse, S., Sang, X., Ovchinnikova, O. S., et al. (2016). Atomisticscale simulations of defect formation in graphene under noble gas ion irradiation. *ACS nano*, 10(9):8376–8384.
- [196] Yoshimura, A. C., Lamparski, M., Kharche, N., and Meunier, V. (2018). Firstprinciples simulation of local response in transition metal dichalcogenides under electron irradiation. *Nanoscale*.
- [197] Yu, Y., Huang, S.-Y., Li, Y., Steinmann, S. N., Yang, W., and Cao, L. (2014). Layer-dependent electrocatalysis of MoS₂ for hydrogen evolution. *Nano letters*, 14(2):553–558.
- [198] Yu, Z., Tetard, L., Zhai, L., and Thomas, J. (2015). Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions. *Energy & Environmental Science*, 8(3):702–730.
- [199] Yuan, L. and Huang, L. (2015). Exciton dynamics and annihilation in WS₂ 2D semiconductors. *Nanoscale*, 7(16):7402–7408.
- [200] Zhang, H., Zhao, Q., Tang, Z., Liu, S., Li, Q., Fan, Z., Yang, F., You, L., Li, X., Zhang, J., et al. (2013a). Slowing down DNA translocation through solid-state nanopores by pressure. *Small*, 9(24):4112–4117.

- [201] Zhang, Y., Liu, L., Sha, J., Ni, Z., Yi, H., and Chen, Y. (2013b). Nanopore detection of DNA molecules in magnesium chloride solutions. *Nanoscale research letters*, 8(1):245.
- [202] Zhang, Y., Zhang, L., and Zhou, C. (2013c). Review of chemical vapor deposition of graphene and related applications. Accounts of chemical research, 46(10):2329–2339.
- [203] Zhang, Z., Yue, C., and Hu, J. (2017). Fabrication of porous MoS₂ with controllable morphology and specific surface area for hydrodeoxygenation. *Nano*, 12(09):1750116.
- [204] Zhao, S., Xue, J., and Kang, W. (2013a). Ion selection of charge-modified large nanopores in a graphene sheet. *The Journal of chemical physics*, 139(11):114702.
- [205] Zhao, W., Ghorannevis, Z., Amara, K. K., Pang, J. R., Toh, M., Zhang, X., Kloc, C., Tan, P. H., and Eda, G. (2013b). Lattice dynamics in mono-and few-layer sheets of WS₂ and WSe₂. *Nanoscale*, 5(20):9677–9683.
- [206] Zhao, W., Ghorannevis, Z., Chu, L., Toh, M., Kloc, C., Tan, P.-H., and Eda, G. (2012). Evolution of electronic structure in atomically thin sheets of WS₂ and WSe₂. ACS nano, 7(1):791–797.
- [207] Zhao, X., Fu, D., Ding, Z., Zhang, Y., Wan, D., Tan, S. J. R., Chen, Z., Leng, K., Dan, J., Fu, W., et al. (2017). Mo-terminated edge reconstructions in nanoporous molybdenum disulfide film. *Nano letters*.

- [208] Zhou, C., Zhao, Y., Raju, S., Wang, Y., Lin, Z., Chan, M., and Chai, Y. (2016). Carrier type control of WSe₂ field-effect transistors by thickness modulation and MoO₃ layer doping. Advanced Functional Materials, 26(23):4223–4230.
- [209] Zhou, Z., Hu, Y., Wang, H., Xu, Z., Wang, W., Bai, X., Shan, X., and Lu, X. (2013). DNA translocation through hydrophilic nanopore in hexagonal boron nitride. *Scientific reports*, 3:3287.
- [210] Zhou, Z., Lin, Y., Zhang, P., Ashalley, E., Shafa, M., Li, H., Wu, J., and Wang, Z. (2014). Hydrothermal fabrication of porous MoS₂ and its visible light photocatalytic properties. *Materials Letters*, 131:122–124.