

## Introduction

Global water scarcity severely impacts much of the world: less than 2% of Earth's water is fresh and accessible, and 1B people have no access to clean water.

Reverse osmosis (RO) desalination is the primary method of freshwater production. However, modern desalination plants are consume large amounts of energy and produce clean water very slowly, and are limited by thick membrane filters.

Nanomembranes, especially nanoporous graphene (NPG), are hypothesized to yield fresh water more quickly and at lower pressures than current membranes. The “wonder material” graphene is a 2D sheet of carbon and is thought to be ideal due to its single-atom-thinness, flexibility, and high mechanical strength. Nano-sized holes in graphene can permit transport of water molecules and block larger  $\text{Na}^+$  and  $\text{Cl}^-$  ions in seawater.

Molecular dynamics simulations (MDS) were applied to find the optimal porosity in NPG that maximizes the membrane's water permeability, but retain its mechanical stability. Laboratory-scale nanoporous graphene samples were then fabricated, characterized, and tested in filtration to determine experimental desalination performances and compare with theoretical results.

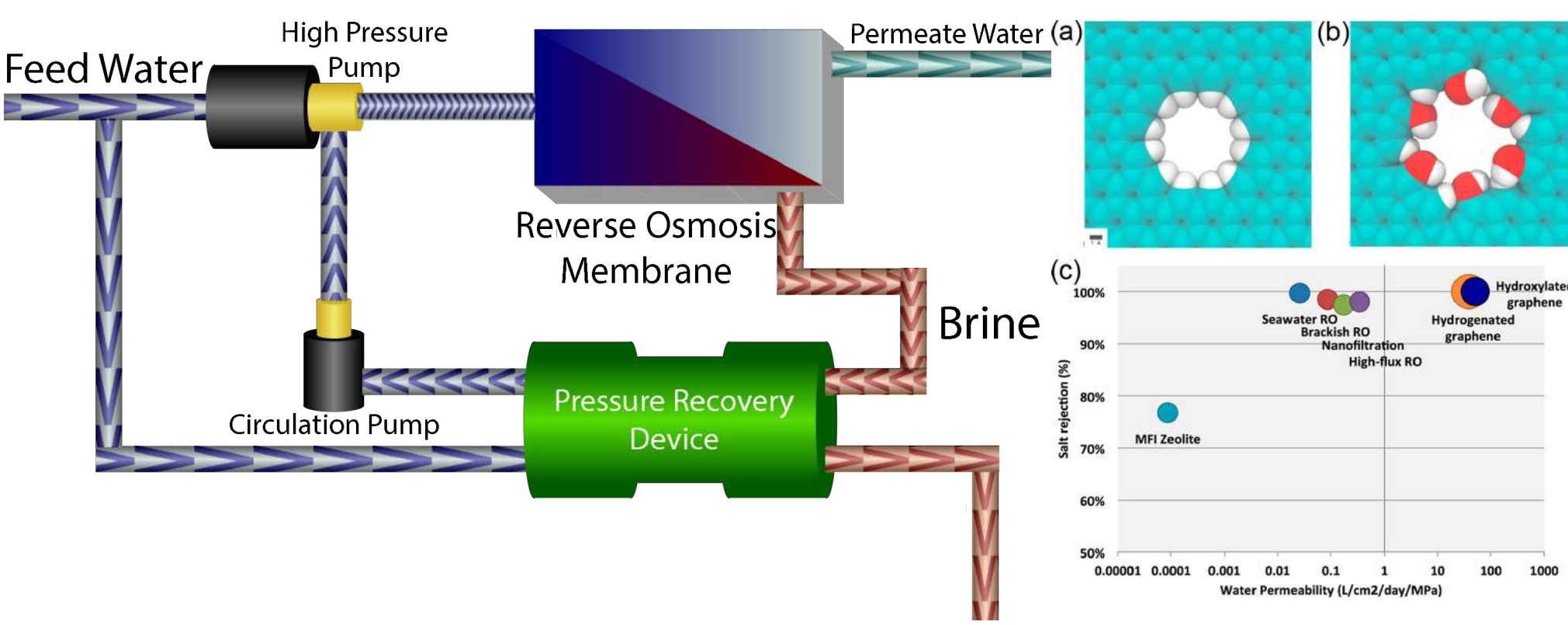
## Background

Current RO systems use polymer membranes, or thin-film composites (TFC), to filter salt ions from pressurized seawater at up to ~250 million gallons per day, but require large applied pressures, which are too expensive in developing regions.

RO performance utilizing nanotechnology has been explored in graphene oxide framework (GOF), carbon nanotube (CNT), graphyne ( $\text{G}^y$ ), and nanoporous graphene (NPG) membranes. All are capable of rejecting salts with variable permeability at 2-3 orders in magnitude greater than TFCs. However, nanomembrane capacity for salt rejection is very limited by mechanical stability.

Computer simulations have demonstrated that hydroxylated NPG membranes can reject salt with up to  $70 \text{ L cm}^{-2} \text{ d}^{-1} \text{ MPa}^{-1}$  in permeability. The hydrophilic nature of the hydroxyl group ( $-\text{OH}$ ) pore lining increases the membrane permeability by two-fold in comparison to hydrogenated NPG. Research indicates that graphene pores must be less than 0.6 nm in size for salt rejection.

Nanoporous graphene membranes have been fabricated mostly for general molecular separation. They have only achieved permeability of  $6 \text{ L cm}^{-2} \text{ d}^{-1} \text{ MPa}^{-1}$  across microscopic regions in forms suitable for desalination. Grain boundaries, intrinsic defects, and tears permit ionic passage and limit scalability in pore fabrication methods, such as ion bombardment or oxygen plasma etching.



### Hypothesis

Maximizing pore density in NPG will increase its water permeability, but even if pores are 0.6 nm, large density will also reduce mechanical stability. This will result in pore deformation and decrease in salt rejection. There is an optimal density for maximal permeability, several orders of magnitude greater than TFCs, with adequate salt rejection. Defect-sealed samples at this porosity will reject salt and demonstrate experimentally similar rates of water permeability.

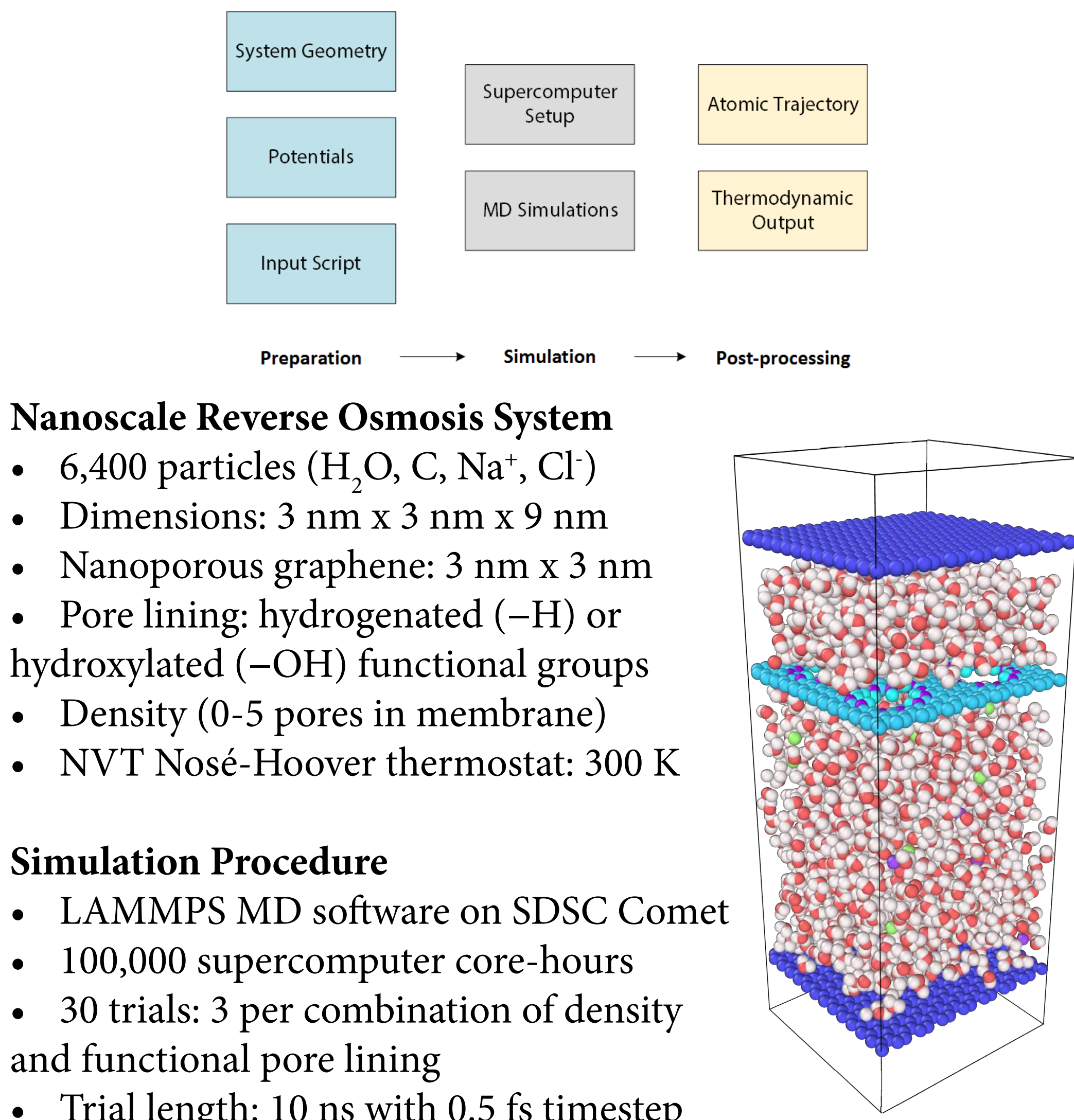
## Software & Computing

- LAMMPS:** MDS package run on supercomputer via console
- Visual Molecular Dynamics:** System geometry generator  
Generated: ionized water, CNT graphene & pistons
- Avogadro:** Selective atomic removal for pore creation
- Pizza.py Toolkit:** Parse/extract data from LAMMPS log file
- Open Visualization Tool:** Simulation renders & animations
- MATLAB** for graphing
- Bash/C++:** Automate generation (simulation & geometries) and compute Lennard-Jones interaction parameters
- High Performance Computer (HPC):** SDSC Comet
  - Linux-based with FTP/SSH access and software packages
  - 4 compute nodes per trial: 45-hour trials on 96 cores
  - Specifications/node: 2.5 GHz dual socket, 12 cores/socket

# Molecular Dynamics Simulation and Experimental Fabrication of Nanoporous Graphene Membranes for Optimal Water Permeability in Reverse Osmosis Desalination

## Molecular Dynamics Simulations

Computer simulation method: applies Newtonian physics in steps to a 3D system of atoms during a nanoscale timeframe.



### Nanoscale Reverse Osmosis System

- 6,400 particles ( $\text{H}_2\text{O}$ , C,  $\text{Na}^+$ ,  $\text{Cl}^-$ )
- Dimensions: 3 nm x 3 nm x 9 nm
- Nanoporous graphene: 3 nm x 3 nm
- Pore lining: hydrogenated ( $-\text{H}$ ) or hydroxylated ( $-\text{OH}$ ) functional groups
- Density (0-5 pores in membrane)
- NVT Nosé-Hoover thermostat: 300 K

### Simulation Procedure

- LAMMPS MD software on SDSC Comet
- 100,000 supercomputer core-hours
- 30 trials: 3 per combination of density and functional pore lining
- Trial length: 10 ns with 0.5 fs timestep

- Static minimization (instantaneous high pressure)
- Equilibration (40-60 picoseconds; 0 MPa on both pistons)
- Piston applied pressure of 32.11 MPa on feed water for 10 ns

### Intermolecular Forces (Force Field Potentials)

- Model most important interactions between every pair of atoms
- AIREBO potential describes C and H membrane atoms
- Water model: TIP4P (accurate, but computationally expensive, electrostatics)
- System-wide: Lennard-Jones and Coulombic parameters

## Experimental Nanofabrication

## Sample Preparation

### Graphene Transfer (1 cm<sup>2</sup> sheet on copper)

- Target substrates: polycarbonate track etch membranes (PCTEM) & silicon wafers
- Mono- and bi- layers adhered to PCTEM
- Spin-coated onto silicon wafers
- Copper etched with APS-100 solution

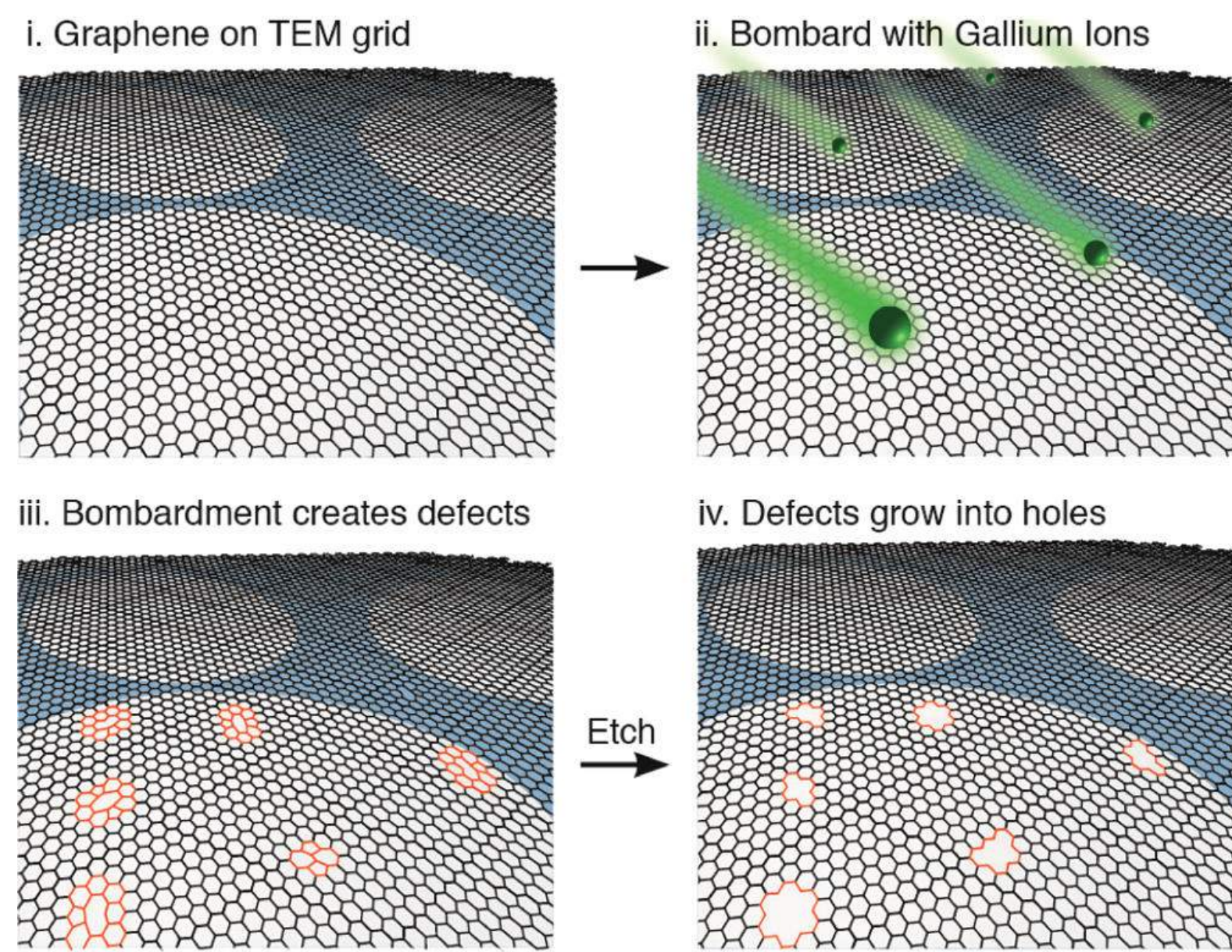
### Atomic Layer Deposition

- Seals defects & grain boundaries (< 10 nm)
- 40 cycles of hafnium oxide deposition (6.13 nm layer)

### Interfacial Polymerization

- Seals tears from transfer (100-200 nm)
- Nylon-6,6 step-growth in Franz cell by reaction of HMDA and adipoyl chloride monomers

## Nanopore Fabrication

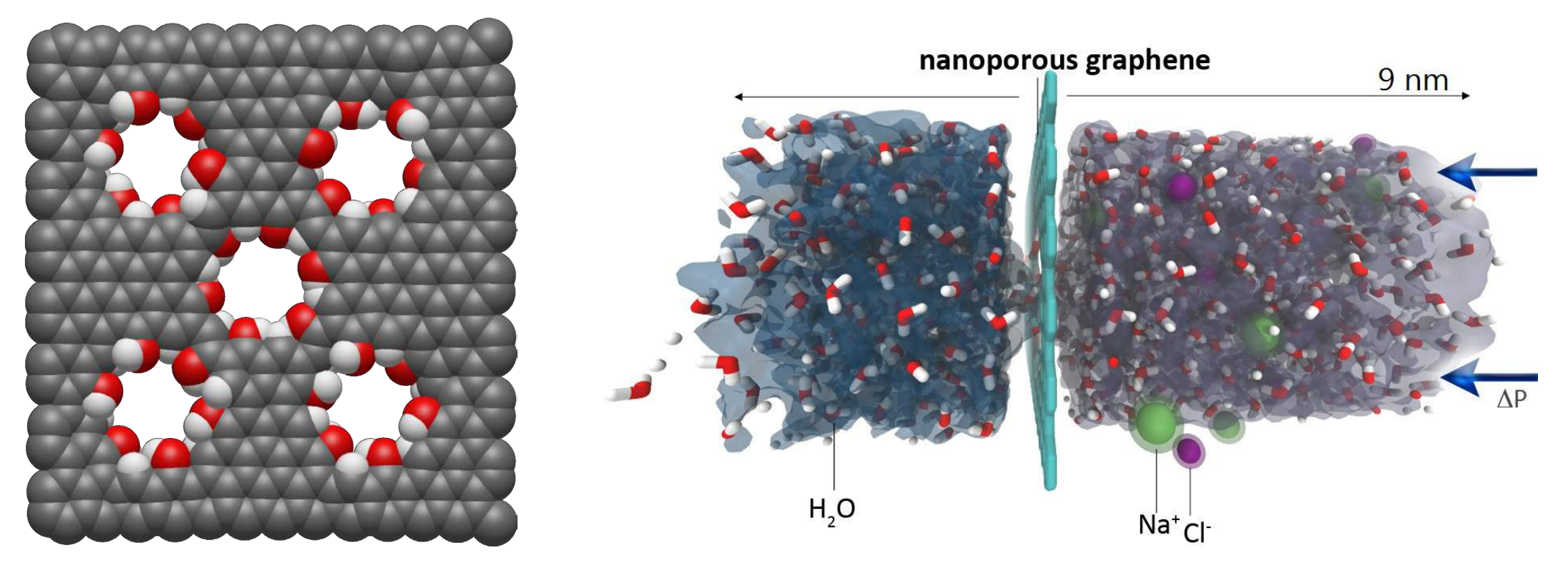


### Gallium Ion Bombardment & Oxidative Etching

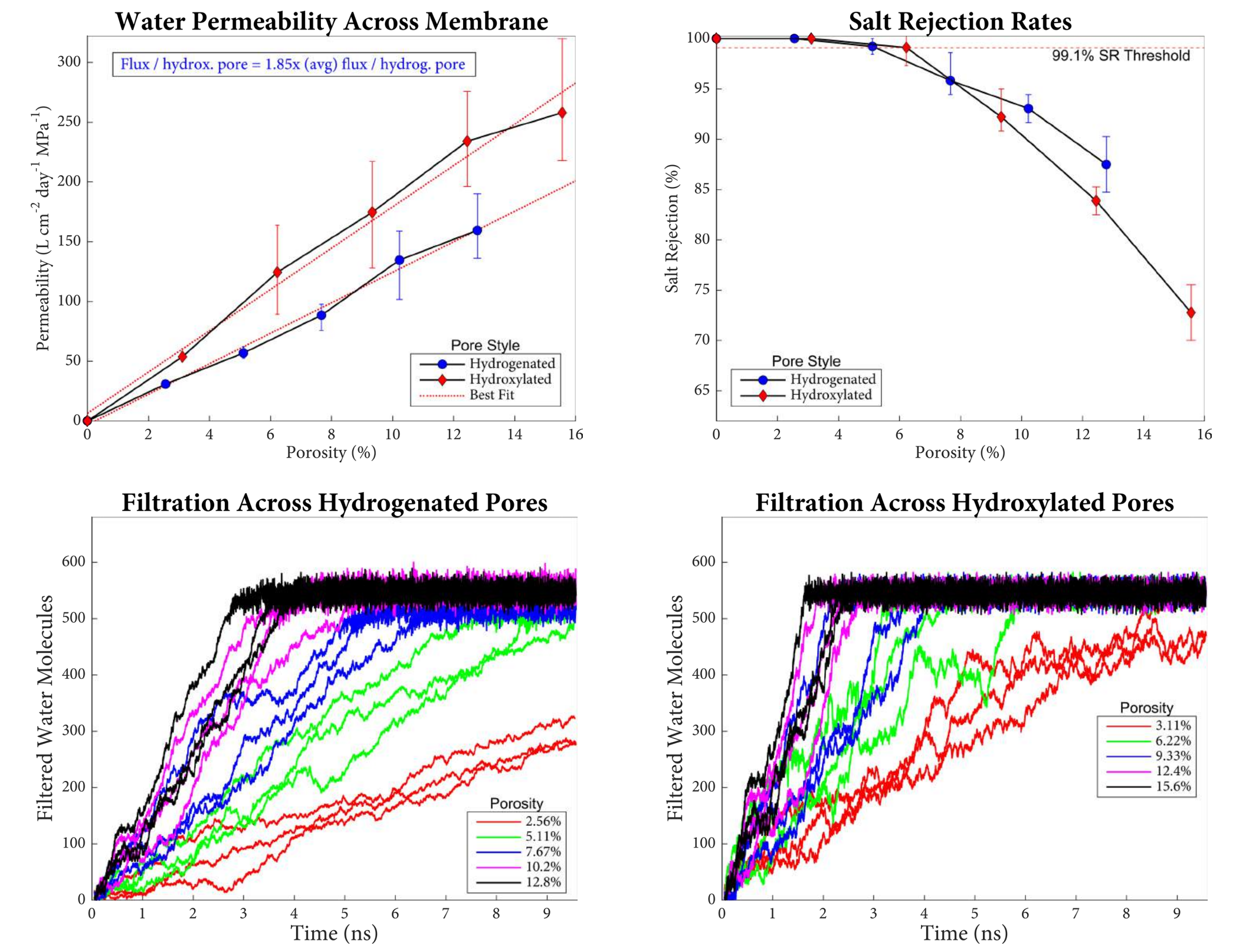
Focused ion beam: bombarded samples at  $10^{12}$  to  $10^{13}$  ions  $\text{cm}^{-2}$   
~85% of impacts created defects  
60 min etch in 1.875mM  $\text{KMnO}_4$  in 6.25%  $\text{H}_2\text{SO}_4$  to grow defects

### Oxygen Plasma Etching

Reactive ion etcher at ~20 W RF power  
Samples exposed for 2-4 seconds



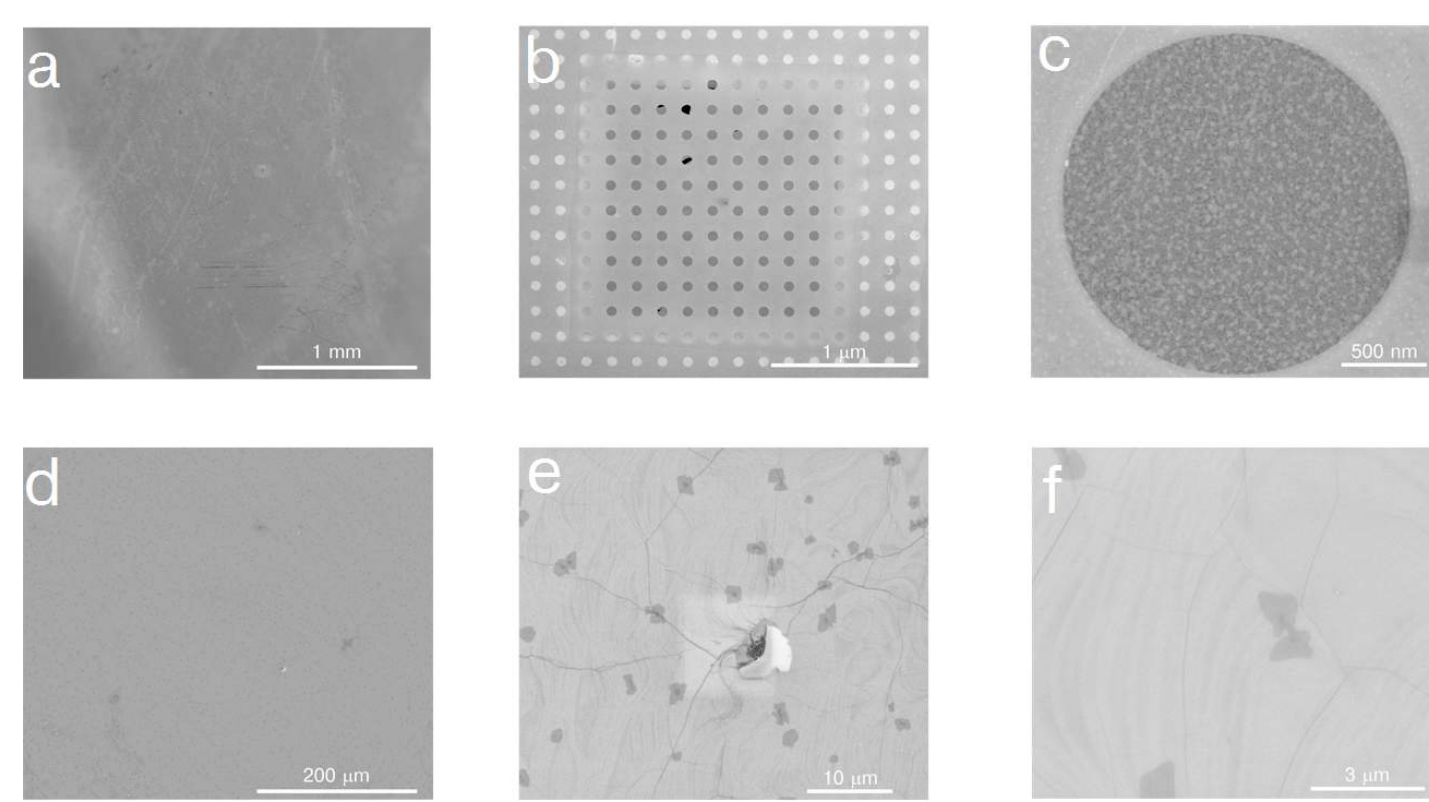
## Computational Data & Calculations



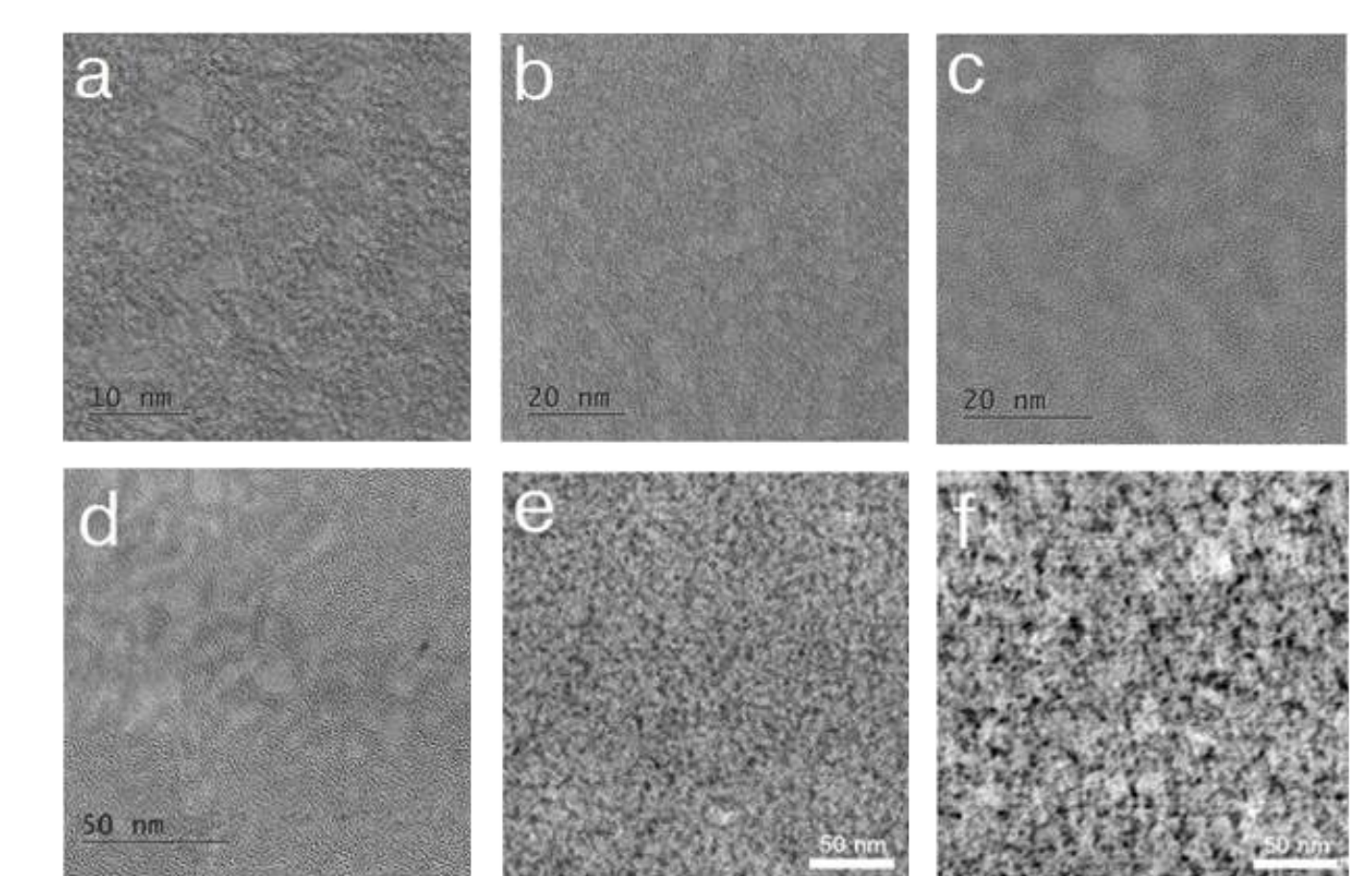
- Porosity:** percentage of total open pore area (proportional to pore count)
- Transmembrane pressure (MPa):** from force on pistons in simulation  
Piston: 416 carbon atoms and 9 square nanometers  
Osmotic pressure ( $\pi$ ): 2.00 MPa ([NaCl] = 0.4428 M) by van'tHoff  
$$F = 0.01 \frac{\text{kcal}}{\text{\AA} \cdot \text{mol}} \rightarrow P = 32.11 \text{ MPa} \quad \pi = iMRT$$
- Water flux ( $\phi$ ):** rate of water molecule filtration in ns<sup>-1</sup>
- Water permeability:** standardized measure of desalination performance as flux per unit pressure and membrane area ( $\text{L cm}^{-2} \text{ d}^{-1} \text{ MPa}^{-1}$ )
- Salt rejection:** percentage of remaining feed region salt ions by time of half water filtration

## Characterization Data

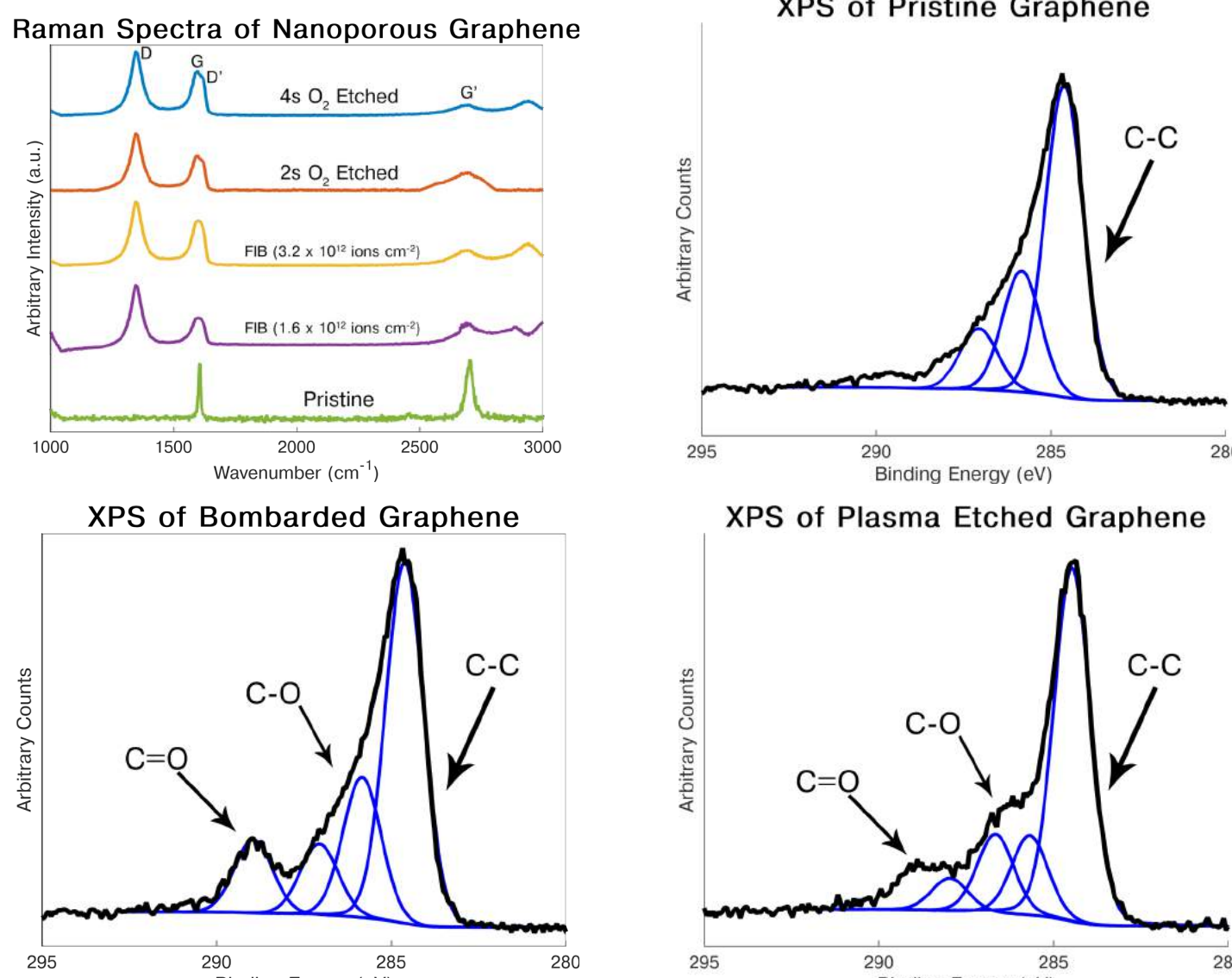
### Scanning Electron Microscopy



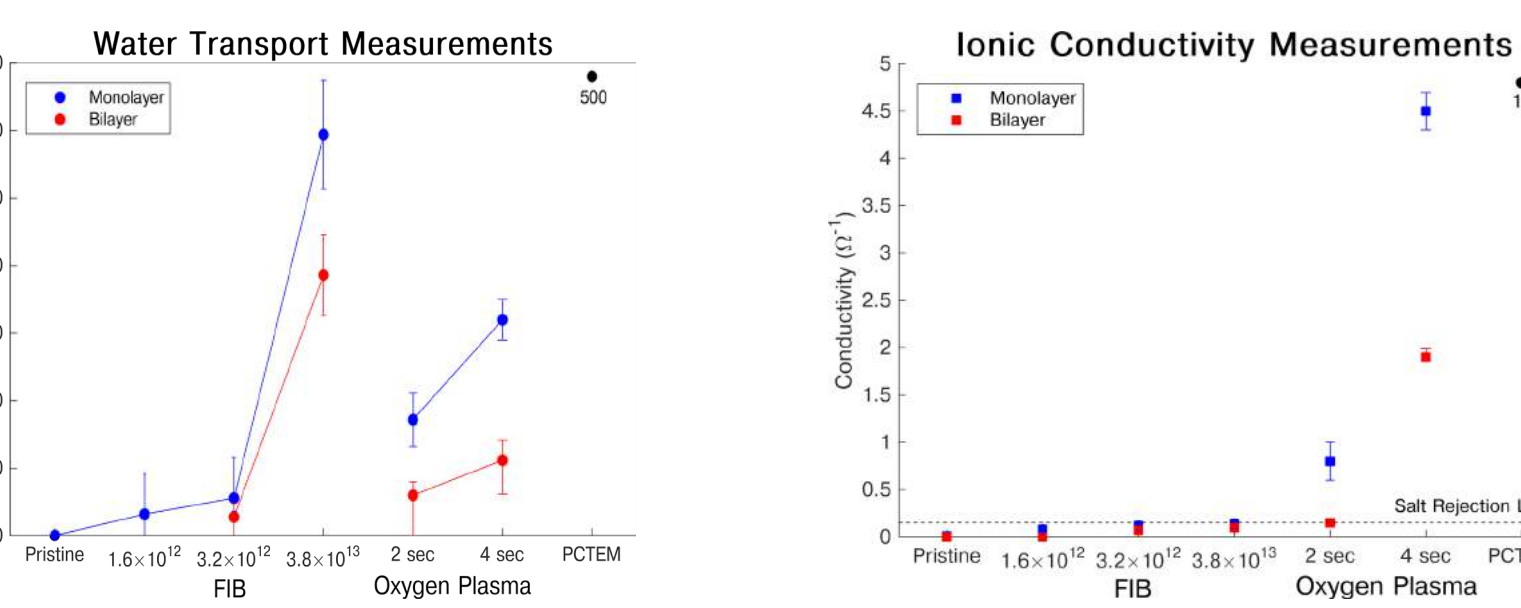
### (Scanning) Transmission Electron Microscopy



### Raman & X-ray Photoelectron Spectroscopy



### Water Transport & Salt Rejection Measurements



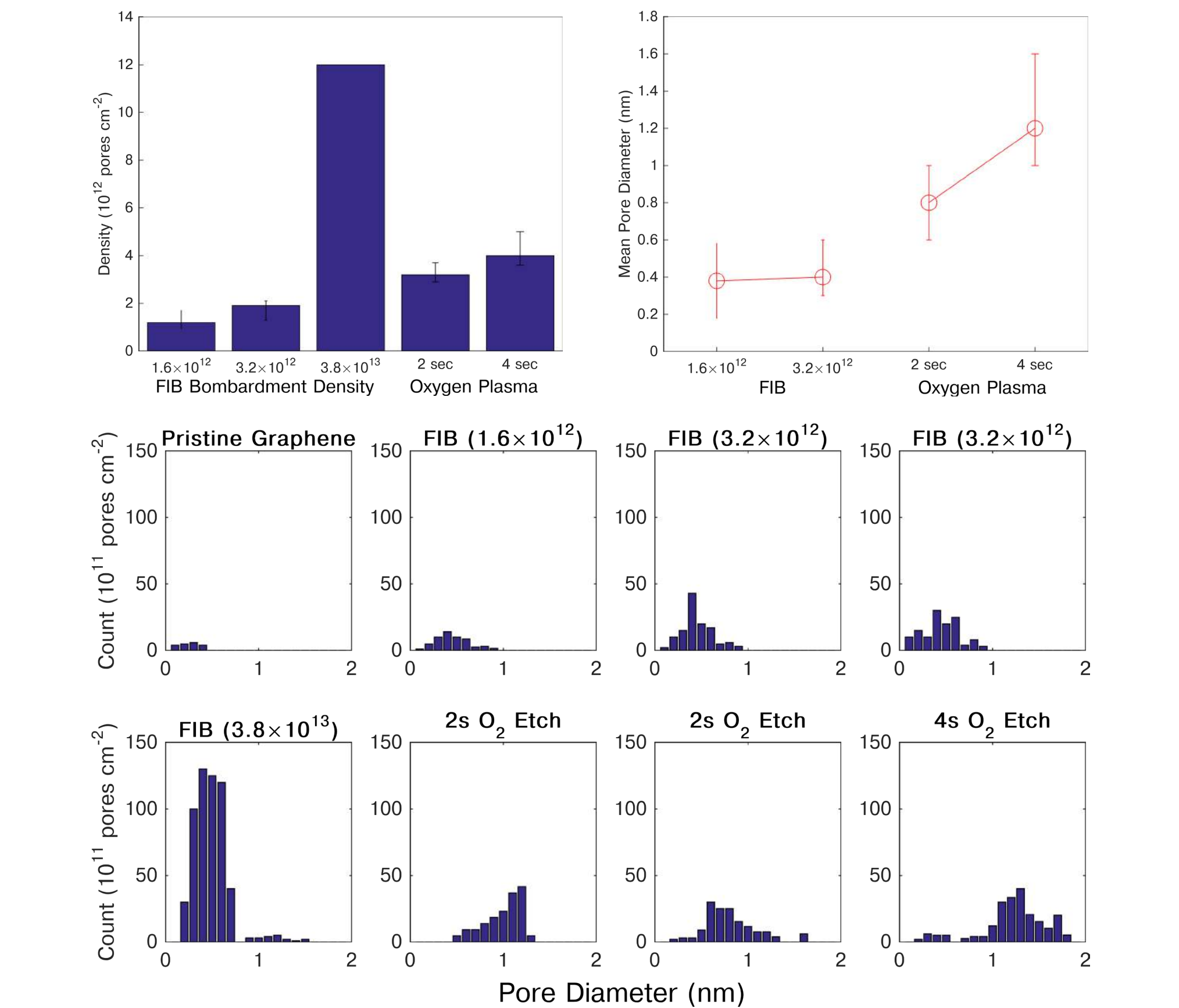
## Sample Count by Method

	Pristine	FIB (ions cm <sup>-2</sup> ): 1.6 x 10 <sup>12</sup>	FIB (ions cm <sup>-2</sup> ): 3.2 x 10 <sup>12</sup>	FIB (ions cm <sup>-2</sup> ): 3.8 x 10 <sup>13</sup>	O <sub>2</sub> Plasma Etching (2s)	O <sub>2</sub> Plasma Etching (4s)
Monolayer PCTEM	3	3	3	2	4	2
Bilayer PCTEM	0	0	2	2	2	2
Silicon Wafers	2	2	2	0	2	2
TEM Grids	1	1	2	1	2	2

## TEM Analysis

### Pore Count, Density & Diameter

Twenty 20,000 nm<sup>2</sup> TEM images were taken for each sample at 80 kV. Pores were distinguished by image processing with the ImageJ software. A Java algorithm was written with a particle analyzer plugin to determine the following pore characteristics.



## Discussion & Conclusion

Reverse osmosis desalination is a primary freshwater production method and implementation of nanotechnology in RO membranes is significant for greater economic feasibility.

Molecular dynamics simulations investigated the effect of modifying pore density and lining on permeability and mechanical stability of NPG. Sheets of mono-/bi- layer NPG were experimentally prepared and fabricated on various substrates, then characterized to determine structure, and tested in a filtration system to compare results against theory. The following conclusions were drawn:

- The optimal structure of NPG is with hydroxylated pores at  $2.22 \times 10^{13}$  pores  $\text{cm}^{-2}$  with permeability of  $125 \text{ L cm}^{-2} \text{ d}^{-1} \text{ MPa}^{-1}$ , which is nearly 5,000 times greater than TFCs.
- Hydroxylated NPG is generally 1.85 times greater in flux and has lower salt rejection than hydrogenated pores.
- Pores fabricated by FIB are desirably sized at ~0.4 nm and can be created at the magnitude of  $10^{13}$  pores  $\text{cm}^{-2}$  in density.
- Defect-sealing approaches surpassed the limitations of grain boundaries, defects, and tears in reduced salt rejection.
- Sample permeability reached  $50 \text{ L cm}^{-2} \text{ d}^{-1} \text{ MPa}^{-1}$ , while rejecting salt, matching theory at that density by 92%.
- Membranes were scalably fabricated to an area of 20 cm<sup>2</sup>, which is 8 magnitudes larger than previously achieved.
- XPS revealed hydroxyl groups formed by both methods.
- Bilayers had greater salt rejection, but lower permeability.

A 30% improvement can be expected in total energy savings, closer to 20% after treatment and since plants already operate at minimum pressures, as well as by 65% in necessary pressure vessels. The energy reduction could equate to a daily savings of \$6,000 in a plant filtering 100,000 m<sup>3</sup> of water per day.

## Further Research

The following related topics and variables could offer further insights and have potential for further study:

- Filtration tests at realistic pressures with long-range strain
- Implementation in RO vessels for pressurized filtration testing over large areas
- Pore fabrication: growth during synthesis, by stitching small sheets together, and by variations in current methods
- Testing other support substrates with greater open pore area
- Methods for and effects of pore functionalization
- MD studies on single-pore deformation
- Other nanomembranes (ex. molybdenum disulfide –  $\text{MoS}_2$ )