# Crystal Growth inside Nanopores

Toward the Preferential Functionalization of Pore Wall

# Overview

- In this preliminary work, the objective is to direct the crystallization inside nanopores of ultrathin SiN membrane.
  - SiN membrane: 50 nm thick
  - Nanopore: 35 nm in diameter
  - Porosity: 15%

- Three types of crystals are being studied
  - Metal-Organic Framework of $\{[\mathrm{Cd}(4,4' - \mathrm{bpy})_2](\mathrm{NO_3})_2\}_n$
  - Calcite $(\mathrm{CaCO_3})$
  - Magnesite $(\mathrm{MgCO_3})$

# Metal-Organic Framework
# $\{[\mathrm{Cd}(4,4' - \mathrm{bpy})_2](\mathrm{NO_3})_2\}_n$

Materials ($\mathrm{Cd}(\mathrm{NO_3})_2 : 4,4' - \mathrm{bpy} = 1:2$ in the unit of mmol)

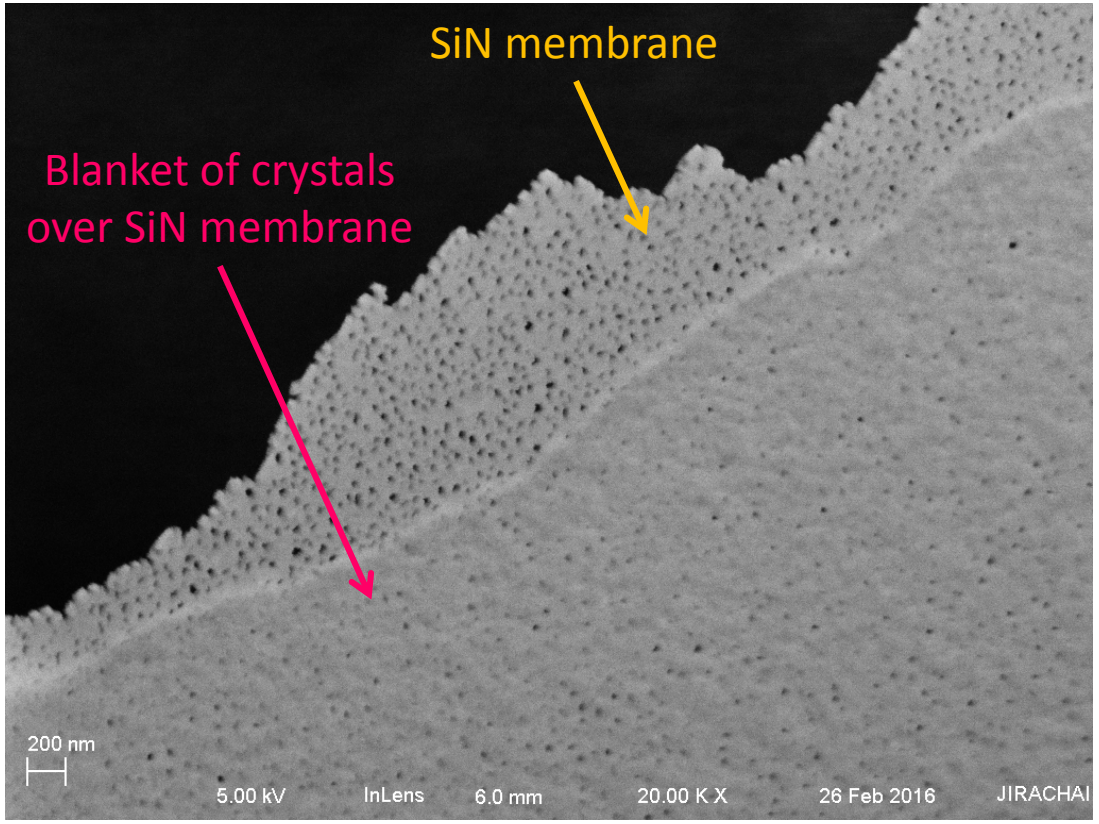
1. Cadmium nitrate tetrahydrate ($\mathrm{Cd}(\mathrm{NO_3})_2 \cdot 4\mathrm{H_2O}$) $MW_{\mathrm{Cd}(\mathrm{NO_3})_2 \cdot 4\mathrm{H_2O}} = 308.48\ \frac{\mathrm{g}}{\mathrm{mol}}$
2. 4,4'-Bipyridyl ($4,4' - \mathrm{bpy}$) $MW_{4,4'-\mathrm{bpy}} = 156.18\ \frac{\mathrm{g}}{\mathrm{mol}}$
3. Ethyl alcohol ($\mathrm{EtOH}$), pure

Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. Preparation, clathration ability, and catalysis of a two-dimensional square network material composed of cadmium(II) and 4,4'-bipyridine. *J. Am. Chem. Soc.* **1994**, 116, 1151-1152.

# Notes

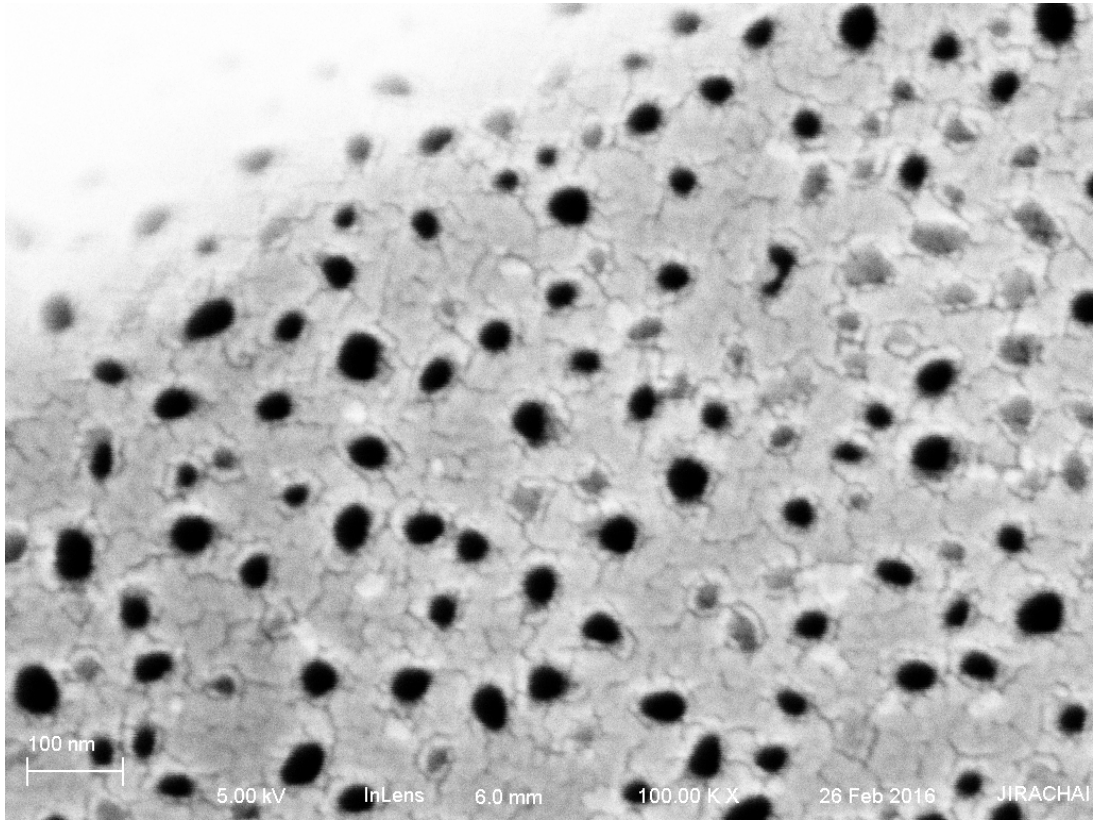
- Membrane side (front side): $4,4' - \mathrm{bpy}$ in $\mathrm{EtOH}$ (anhydrous)
- Groove side (back side): $\mathrm{Cd(NO_3)_2(aq)}$
- All windows of membrane survived the process, but being broken intentionally for SEM imaging.

# Blanket of Crystals Formed on the Front Side of Membrane



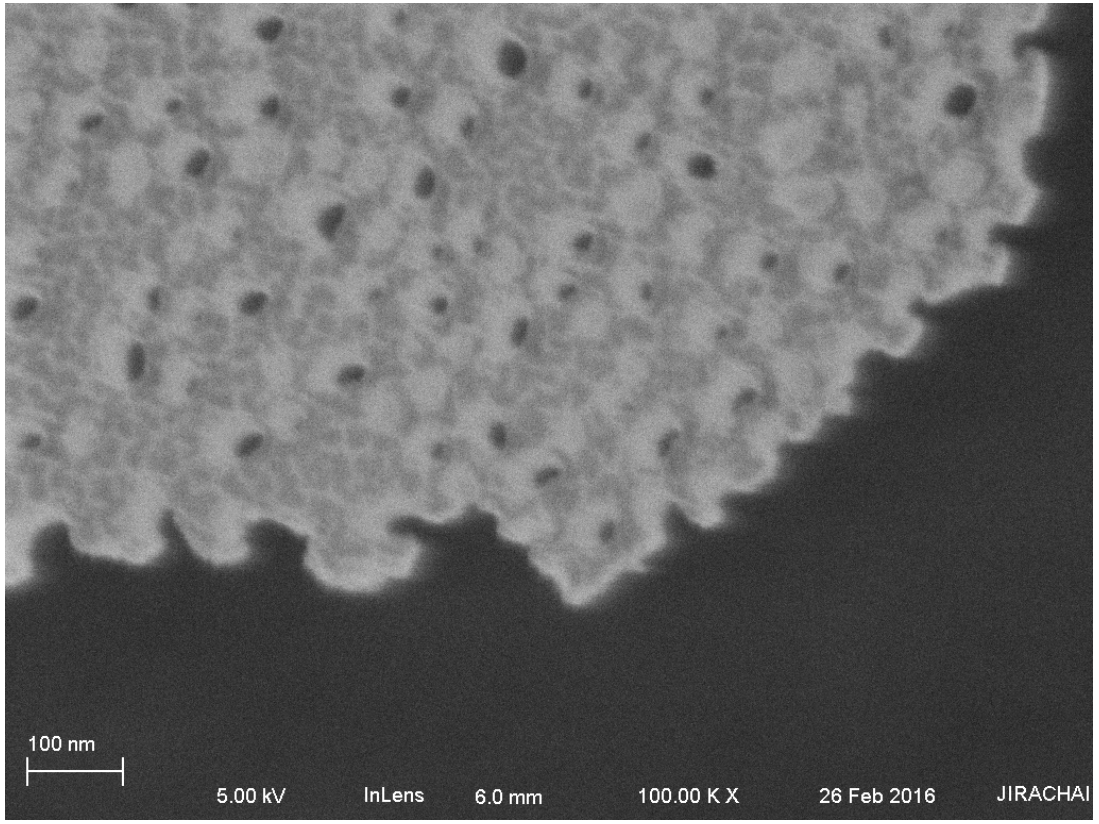

- The blanket of crystals was damaged during the breakage of membrane for SEM imaging; it might not be possible to determine whether the crystals had grown inside its nanopores using this method.
- The blanket was riddled with pin holes.

# Some Nanopores Appeared to Be Filled



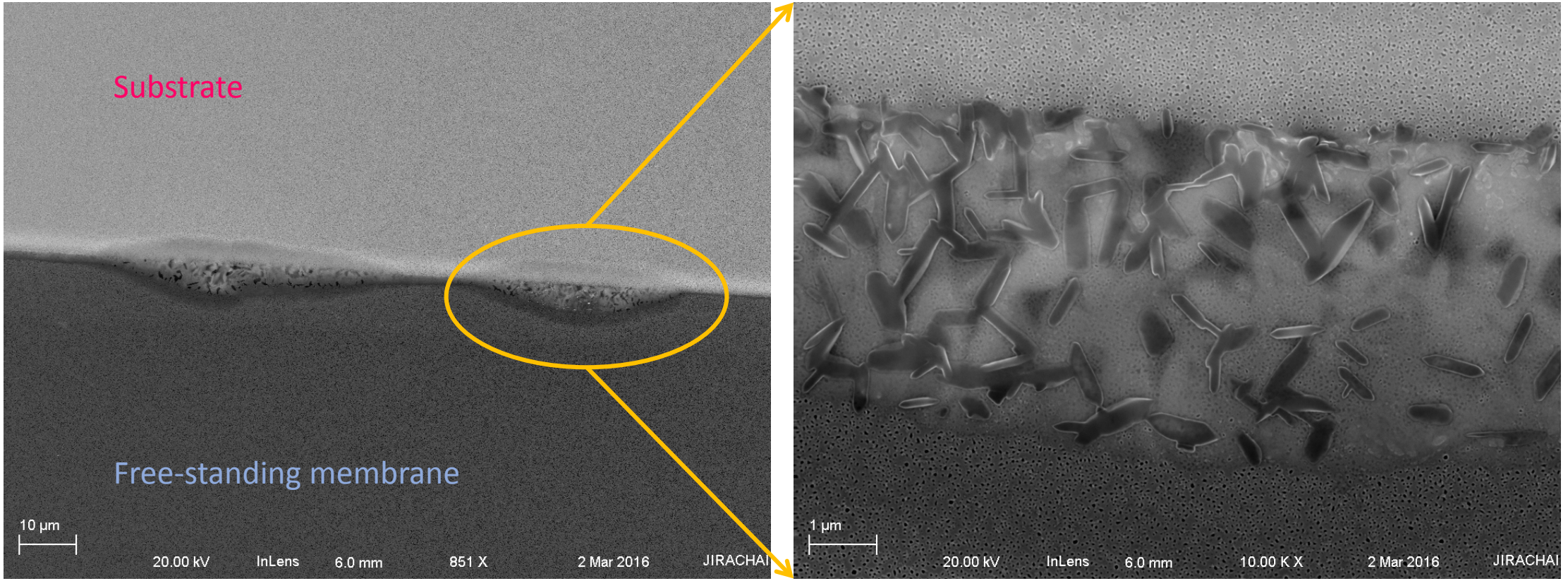

- The texture on the surface of membrane indicated the presence of nanoparticles.
- It appears that they also filled in some of nanopores.

# Back Side of Membrane Showing Crystals around the Mouth of Nanopores

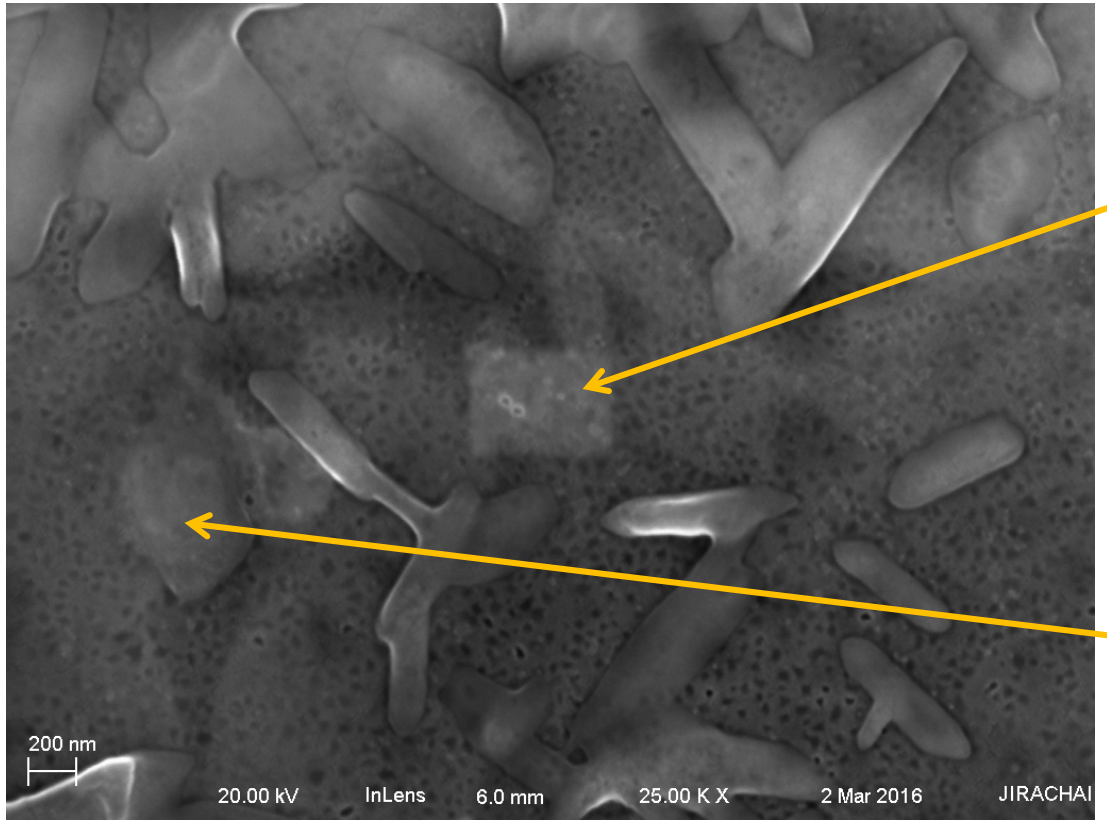


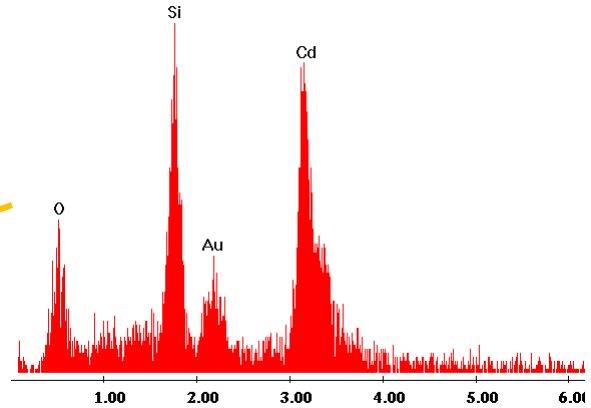

- A view from the back side of another membrane showed many occluded nanopores.
- All nanopores appear to have nanoparticles around their entrance.

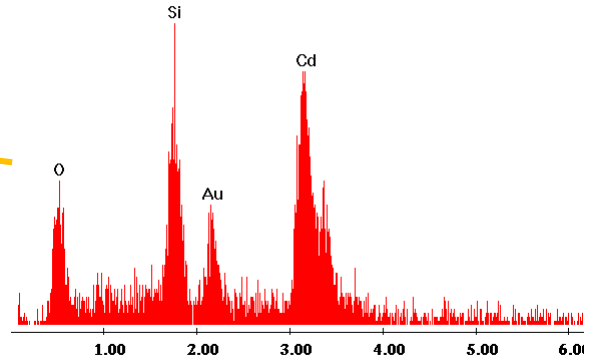
# EDS Showing Significant Cd Peak along Membrane Boundary



# $Cd(NO_3)_2$ and MOF Crystals



# Discussion

- Crystals were possibly formed inside the nanopores as evidenced by the occluded nanopores.

# Calcite

$$CaCl_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaCl(aq)$$

100 mM 100 mM

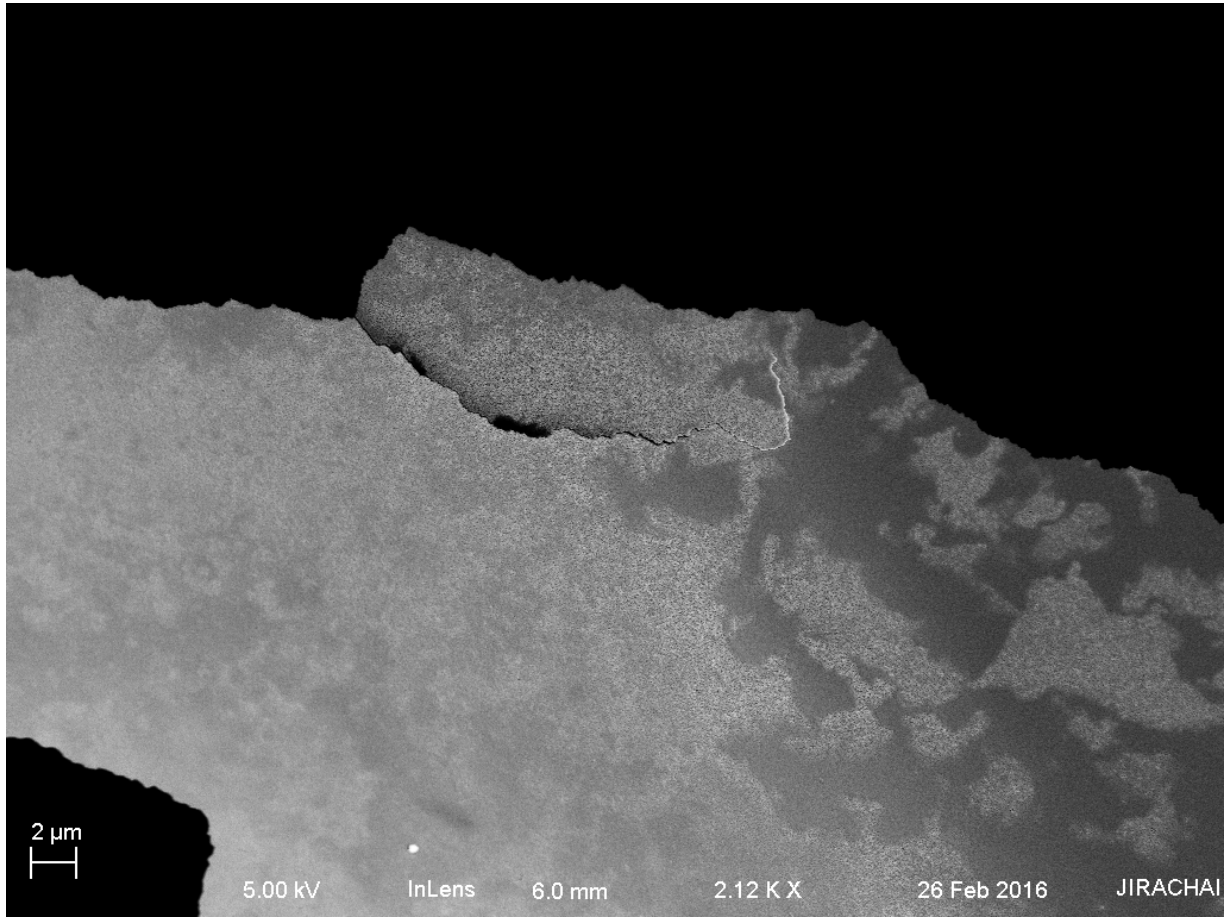
Materials ($CaCl_2 : Na_2CO_3 = 1:1$)

1. Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) $MW_{CaCl_2 \cdot 2H_2O} = 147.01 \frac{g}{mol}$
2. Sodium carbonate ($Na_2CO_3$) $MW_{Na_2CO_3} = 105.99 \frac{g}{mol}$

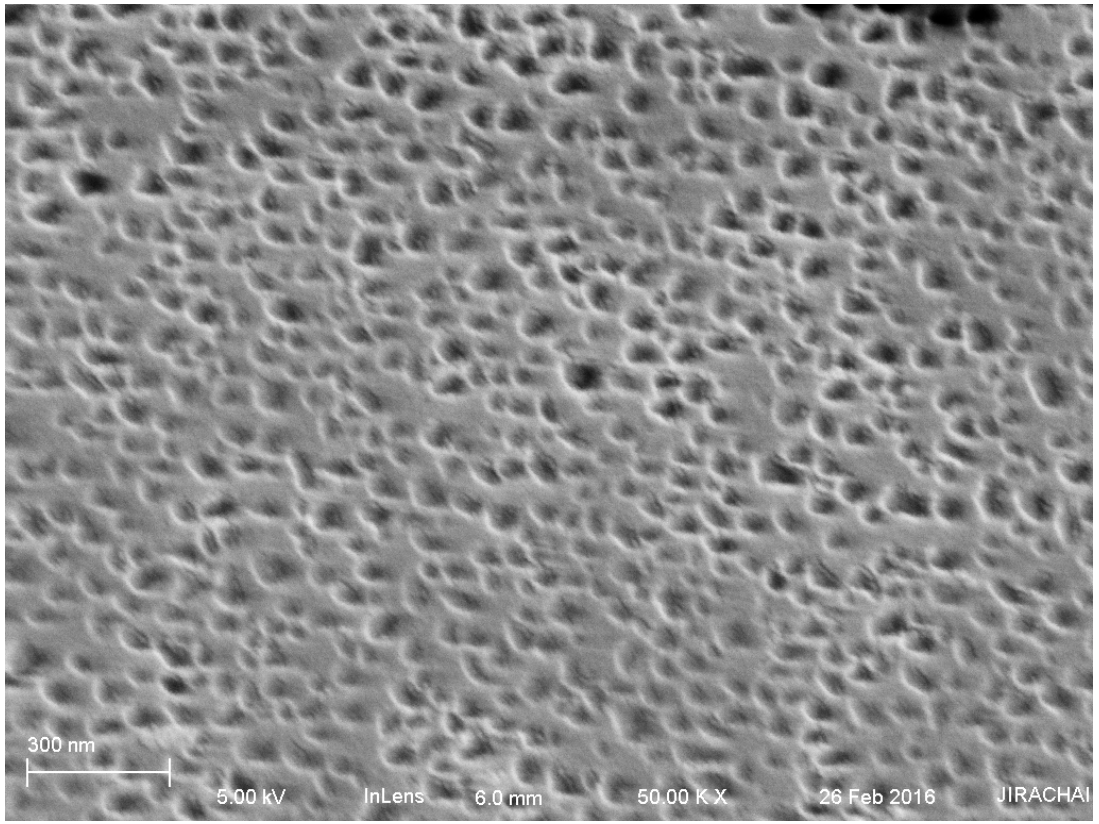
# Notes

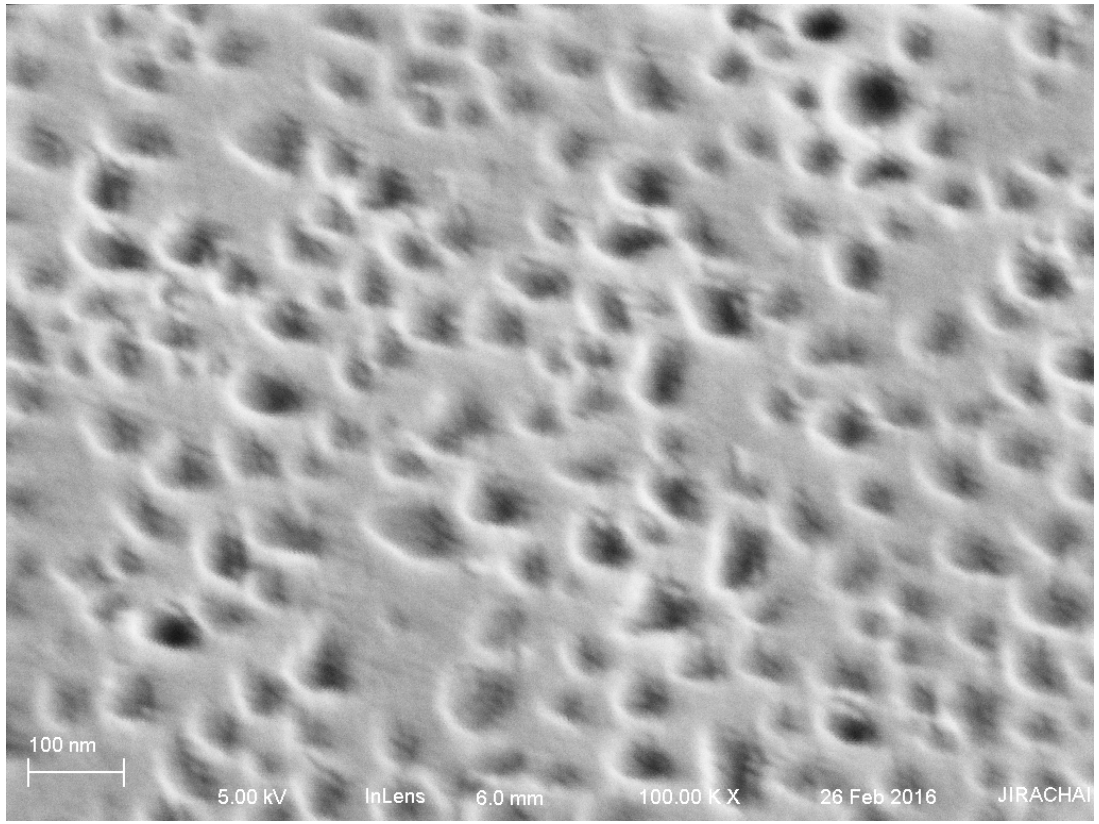
- Membrane side (front side): 100 mM $\mathrm{CaCl_2(aq)}$
- Groove side (back side): 100 mM $\mathrm{Na_2CO_3(aq)}$
- All windows of membrane survived the process, but being broken intentionally for SEM imaging.

# Patterns on Membrane Suggesting the Presence of Crystals



# Crystals inside Nanopores




A majority of nanopores were filled by nanoparticles. They were on the surface of membrane as well

# Discussion

- It is expected that by reducing the reaction time or lowering the concentration of solution, the growth of crystal can be confined within the nanopores.

- Need EDAX to identify the crystals.

# Magnesite

$$MgCl_2(aq) + Na_2CO_3(aq) \rightarrow MgCO_3(s) + 2NaCl(aq)$$

100 mM 100 mM

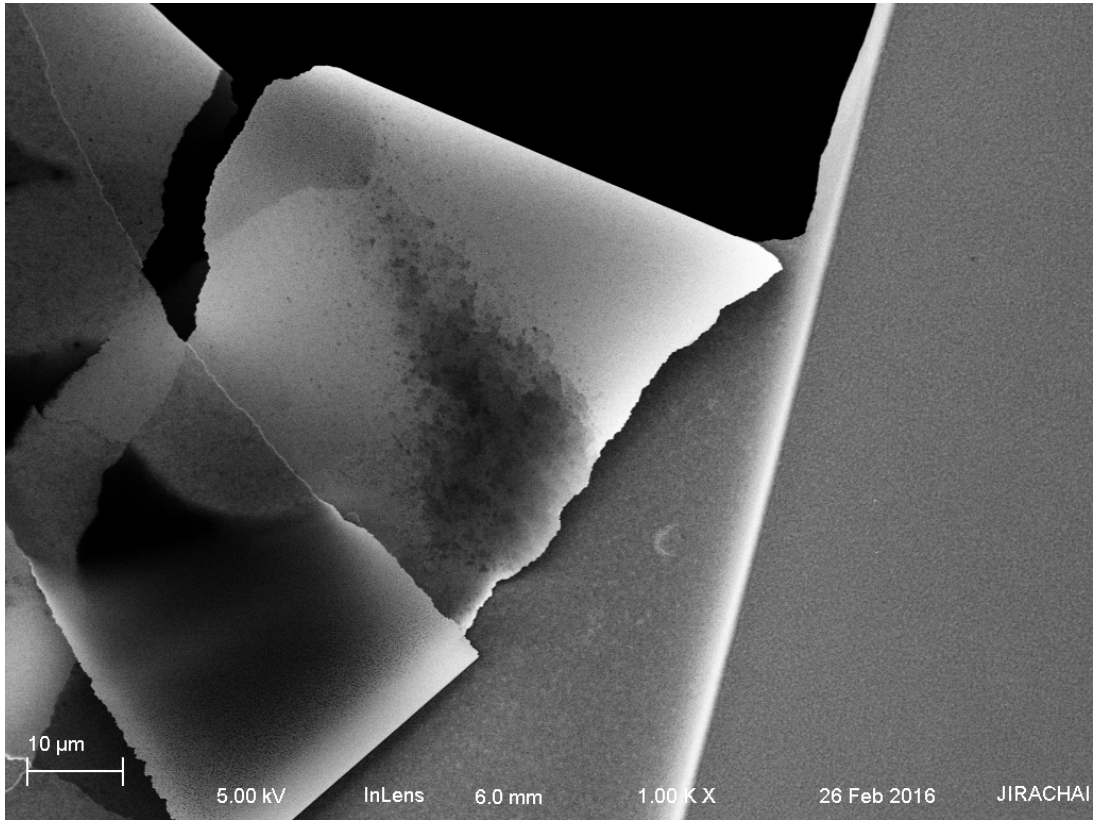
Materials ($MgCl_2 : Na_2CO_3 = 1:1$)

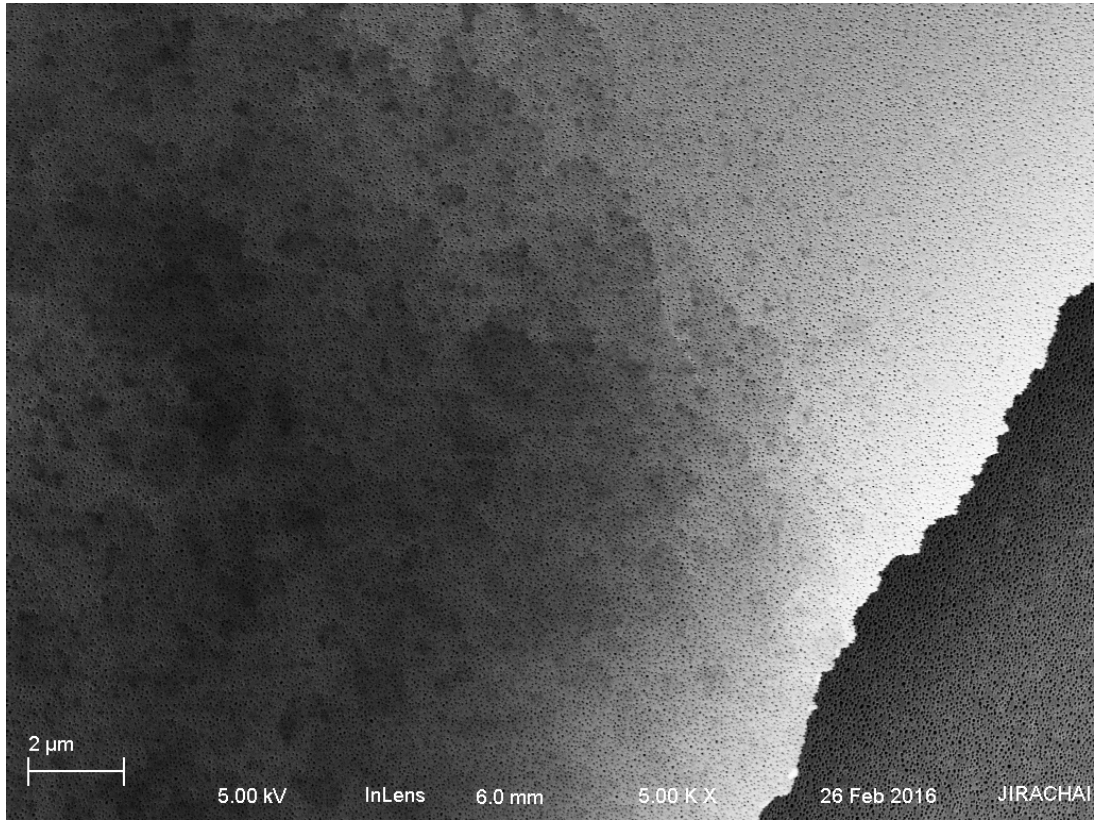
1. Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) $MW_{MgCl_2 \cdot 6H_2O} = 203.30 \frac{g}{mol}$
2. Sodium carbonate ($Na_2CO_3$) $MW_{Na_2CO_3} = 105.99 \frac{g}{mol}$

# Notes

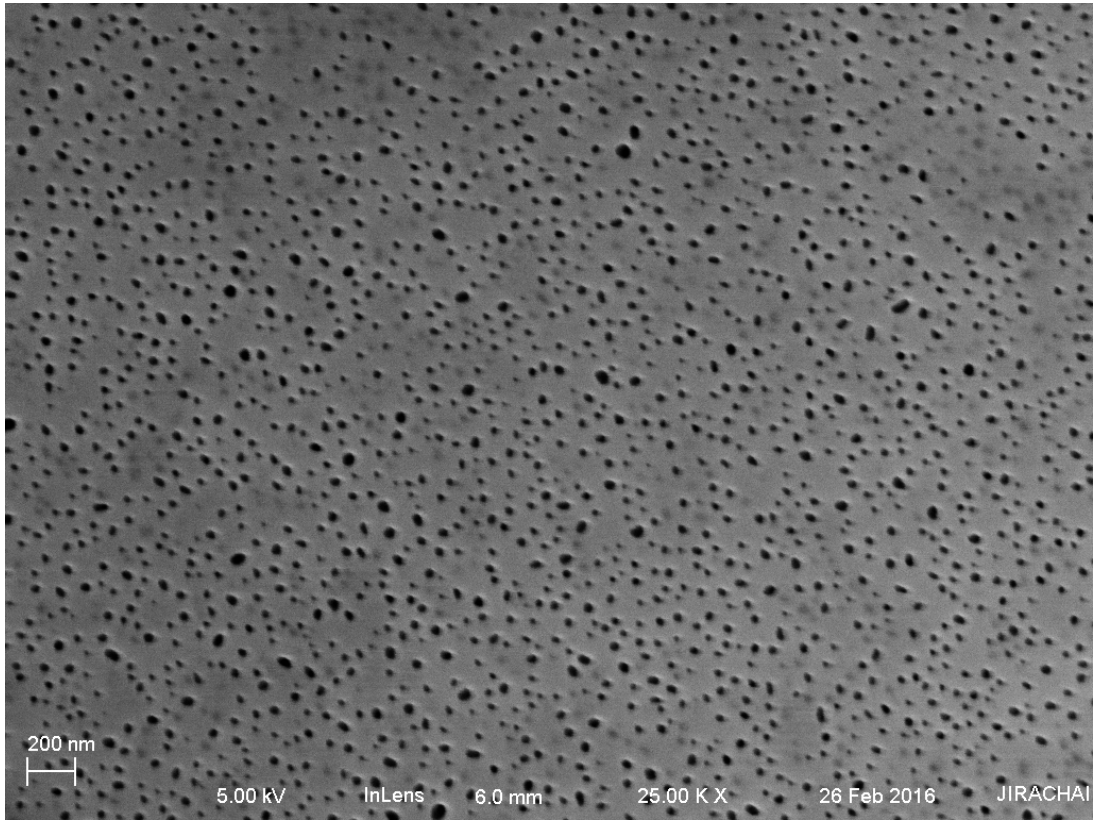
- Membrane side (front side): 100 mM $\mathrm{MgCl_2(aq)}$
- Groove side (back side): 100 mM $\mathrm{Na_2CO_3(aq)}$
- Three out of five windows of membrane were completely broken and the rest were partially broken while soaking in DI water to remove the excess reagents and NaCl by-product.

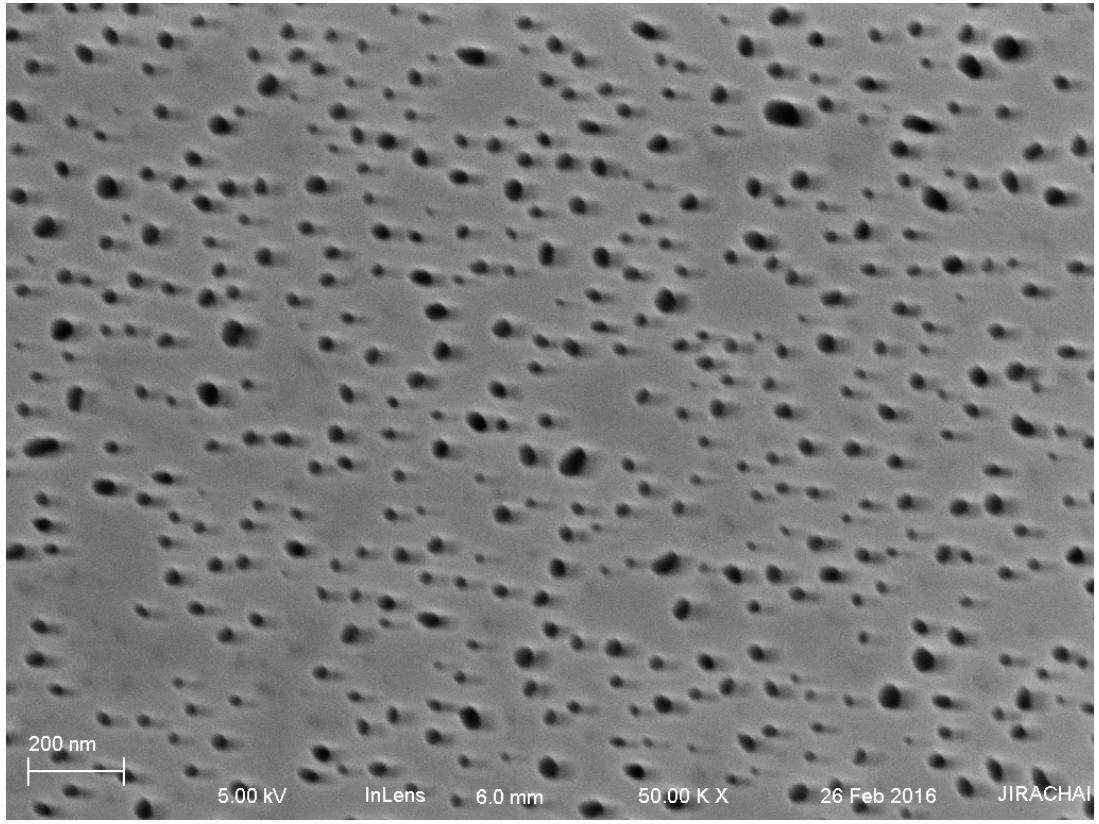
# Patterns on Membrane Suggesting the Presence of Crystals



# Occluded Nanopores beneath Smooth Layers of Fine Crystals?



# Discussion

- It appears that the surface of membrane was covered by smooth layers of nanoparticles. The occluded nanopores could be observed beneath such layers.

- Need to repeat the experiment to find out why most of the windows of membrane were broken while soaking in DI water. It was under the similar conditions as for calcite crystals, but all membranes survived.

- Again, need EDAX to identify the nanoparticles.