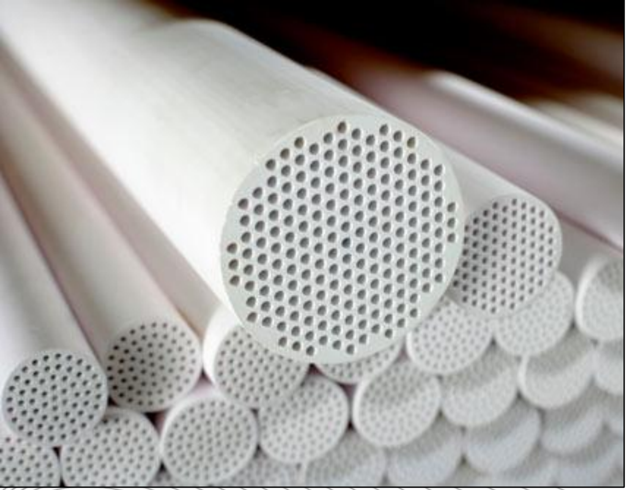


Tuning ceramic nanofiltration membranes by atmospheric-pressure MLD grown titanicone layers

F. Roozeboom
Faculty of Science & Technology, University of Twente, The Netherlands

Co-authors & Acknowledgments

Harpreet Sondhi
PhD Candidate, Inorganic Membranes, UTwente, Enschede

Dr. Mingliang Chen
Post-Doc, Dept. of Chem. Engineering, TU Delft, Delft

Michiel P. Nijboer
PhD Candidate, Inorganic Membranes, UTwente, Enschede

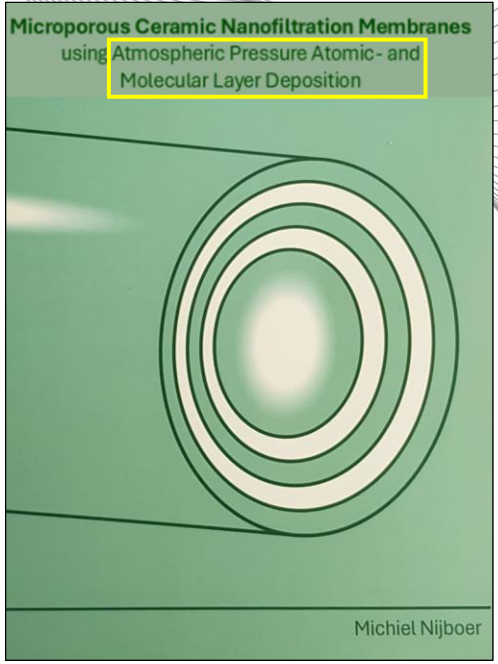
Prof. Arian Nijmeijer
Full Prof., Inorganic Membranes, UTwente, Enschede

Dr. Alexey Y. Kovalgin
Associate Prof., Integrated Devices and Systems, UTwente, Enschede

Dr. M. Luiten-Olieman
Prime Investigator, Inorganic Membranes, UTwente, Enschede

Dr. Mikhael Bechelany Institut Européen des Membranes Université Montpellier, France

- H. Sondhi, et al., ***Molecular layer deposited*** *metalcone hybrid layers for solvent-resistant nano-filtration membranes: surface wetting and permeation*, submitted.
- M.P. Nijboer, PhD thesis University of Twente, Netherlands, Sept. 8, 2025 ....
- M.P. Nijboer, et al., *Influence of calcination temperature on the physico-chemical properties of* ***ALD*** */* ***MLD*** *hybrid inorganic/organic ceramic nanofiltration membranes*; Open Ceramics, **22**, 100795 (2025)
- H. Sondhi, et al., *Ceramic nanofiltration membranes: creating nanopores by calcination of atmospheric-pressure* ***MLD*** *grown titanicone layers,* Membranes, **15**(3) 86 (2025)
- H. Sondhi, et al., *Increasing hydrophobicity of ceramic membranes by post-deposition nitrogen annealing of* ***MLD*** *grown hybrid layers*, Applied Surface Science, 683, Part A, 161790 (2025)
- M.P. Nijboer, et al., *Tuning Nanopores in Tubular Ceramic Nanofiltration Membranes with Atmospheric-Pressure* ***ALD****: Prospects for Pressure-Based In-line Monitoring of Pore Narrowing*, Separations, **11**(1), 24 (2024)
- M. Chen, et al., *Atmospheric-Pressure* ***ALD****: recent applications and new emerging applications in high porosity/ 3D materials*, Dalton Transactions, **52**(10), 10254–10277 (2023)



Institut Européen des Membranes
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LENNTECH Water Treatment Solutions
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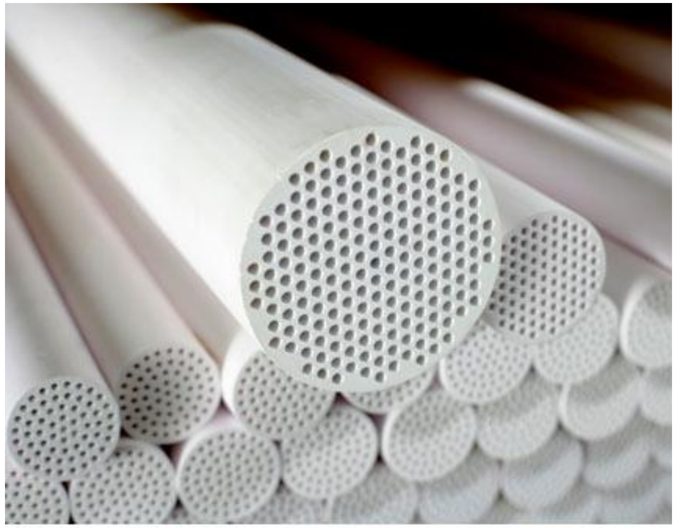
atech innovations gmbh
Institute for Sustainable Process Technology
UNIVERSITY OF TWENTE.

Ceramic Membranes - industrial applications



www.atech-innovations.com

coorstek.com

www.metawater.co.jp

pwntechnologies.com

300 m^3/h ultrafiltration used in Grundmühle waterworks (Germany)
(3 olympic swimming pools/day)

Membranes - industrial applications

Metal industry / Surface engineering:
- Recycling and disposal of degreasing and rinsing bathes
- Treatment of **oil/water emulsions**
- Recovery of heavy metals
- Cleaning of wastewater from grinding processes

Food and beverages
- Clarification of **juice and beer**
- Sterilization of milk and whey
- Dewatering of products

Purifying & concentrating

Chemical industry:
- Concentration of polymer suspensions and metal hydroxide solutions
- Separation of **catalysts**
- Recovery of dyes and pigments
- Cleaning and recycling of organic solvents

Recycling and environment
- Oil/water separation
- Recovery of **pharmaceuticals and pesticides**
- Retention of heavy metals and radioactive substances
- Purification of the drain of sewage plants

Textiles / Pulp and paper industry:
- Concentration, fractionation, isolation and sterilization for **antibiotics, enzymes, proteins, and vitamins**
- Separation, concentration and dewatering of biomass and algae
- Disposal of fat emulsions
- Separation of yeast

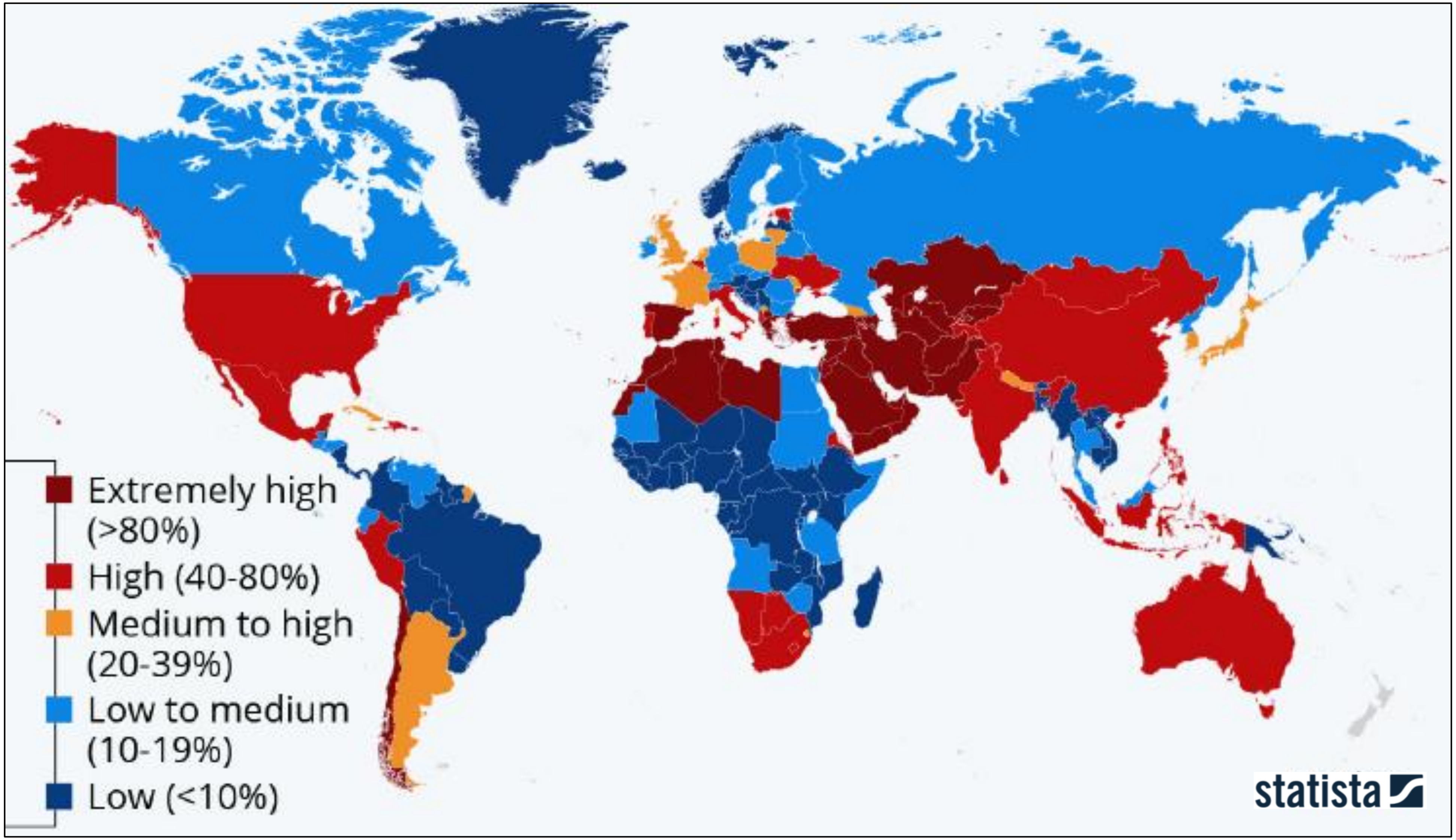
State-of-the-art in industry: Mostly polymer membranes:

Low-cost, scalable, tunable porosity

Not robust at high temperatures, harsh chemistry, extreme pH
► **Swelling**

► **Can we develop inorganic, ceramic membranes by ALD/ MLD for lower energy alternatives with minimal carbon footprint?**

Water withdrawal / supply ratio in 2040



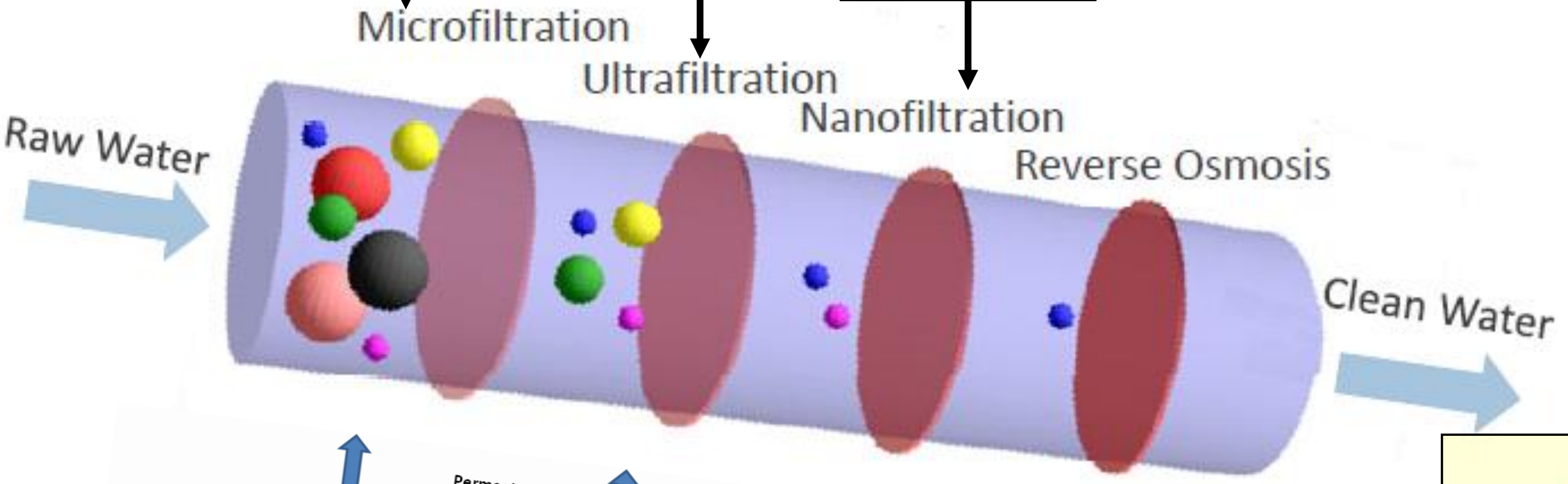
➡ Urgent need or low-cost, scalable nanofiltration membranes for water purification

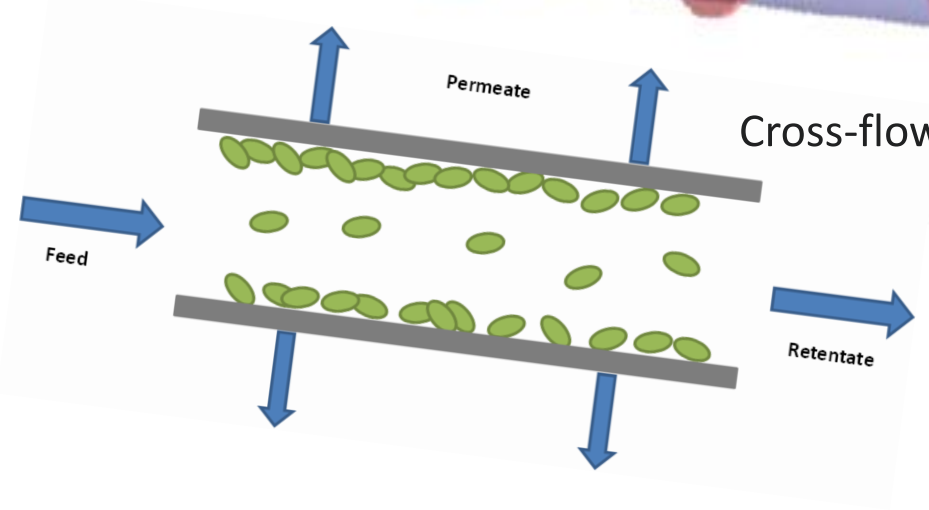
Ceramic Membranes – for purifying and concentrating solutions

Macromolecules ($>10^6$ Da)

Micron-sized molecules (10^3 - 10^6 Da)

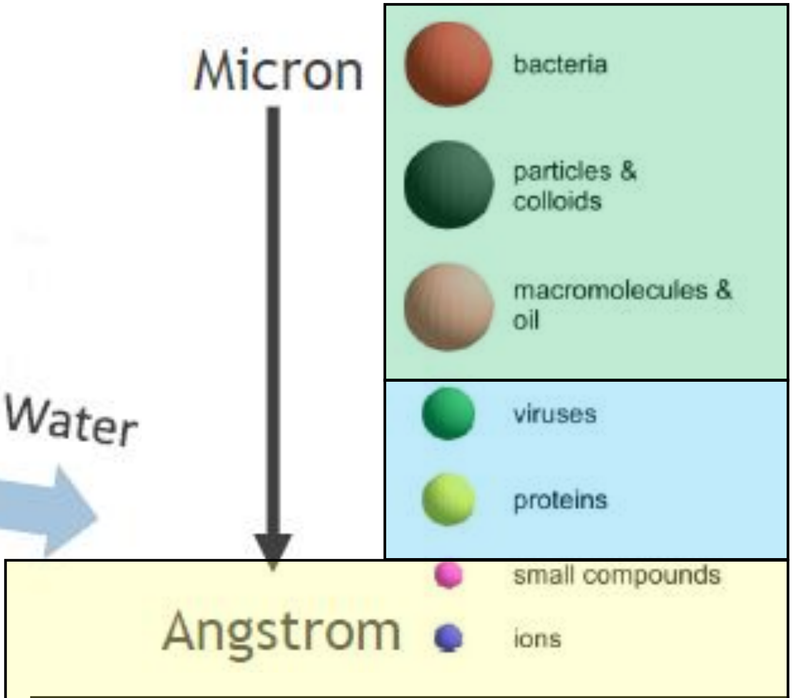
Nano-sized molecules (10^2 - 10^3 Da)

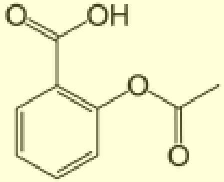




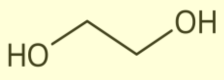
Cross-flow operation

Size-selective meshes





aspirin, $C_9H_8O_4$:
~ 190 Da
Diameter ~ 1 nm

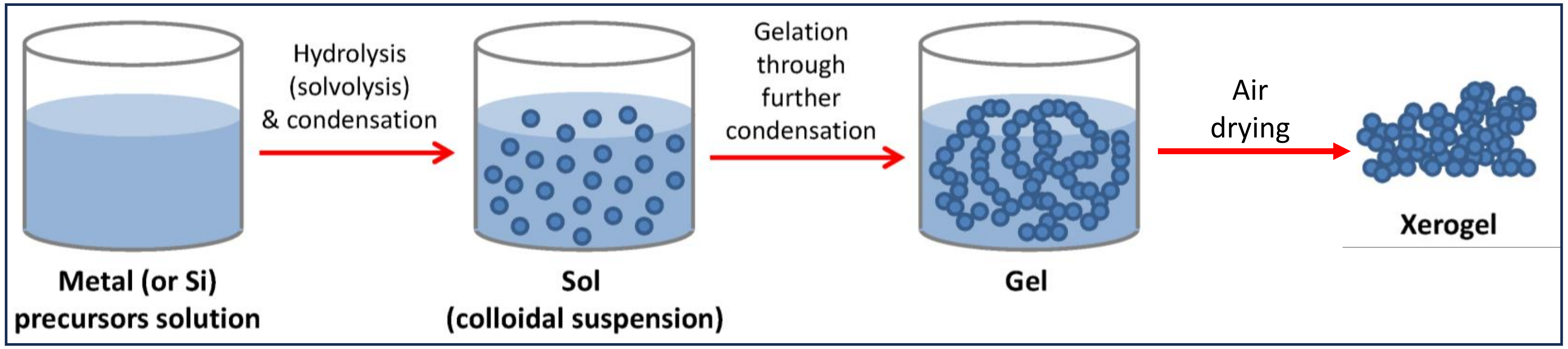


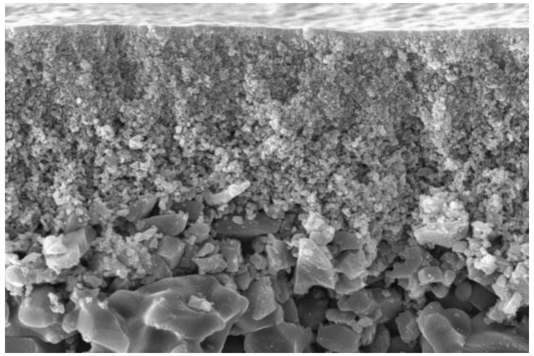
ethylene glycol, $C_2H_6O_2$:
~ 62 Da
Diameter ~ 0.44 nm

Production of ceramic membranes

State-of-art: Sol-gel and Extrusion technology

Sol-gel coating & drying …





https://inopor.com

Extrusion

https://inopor.com

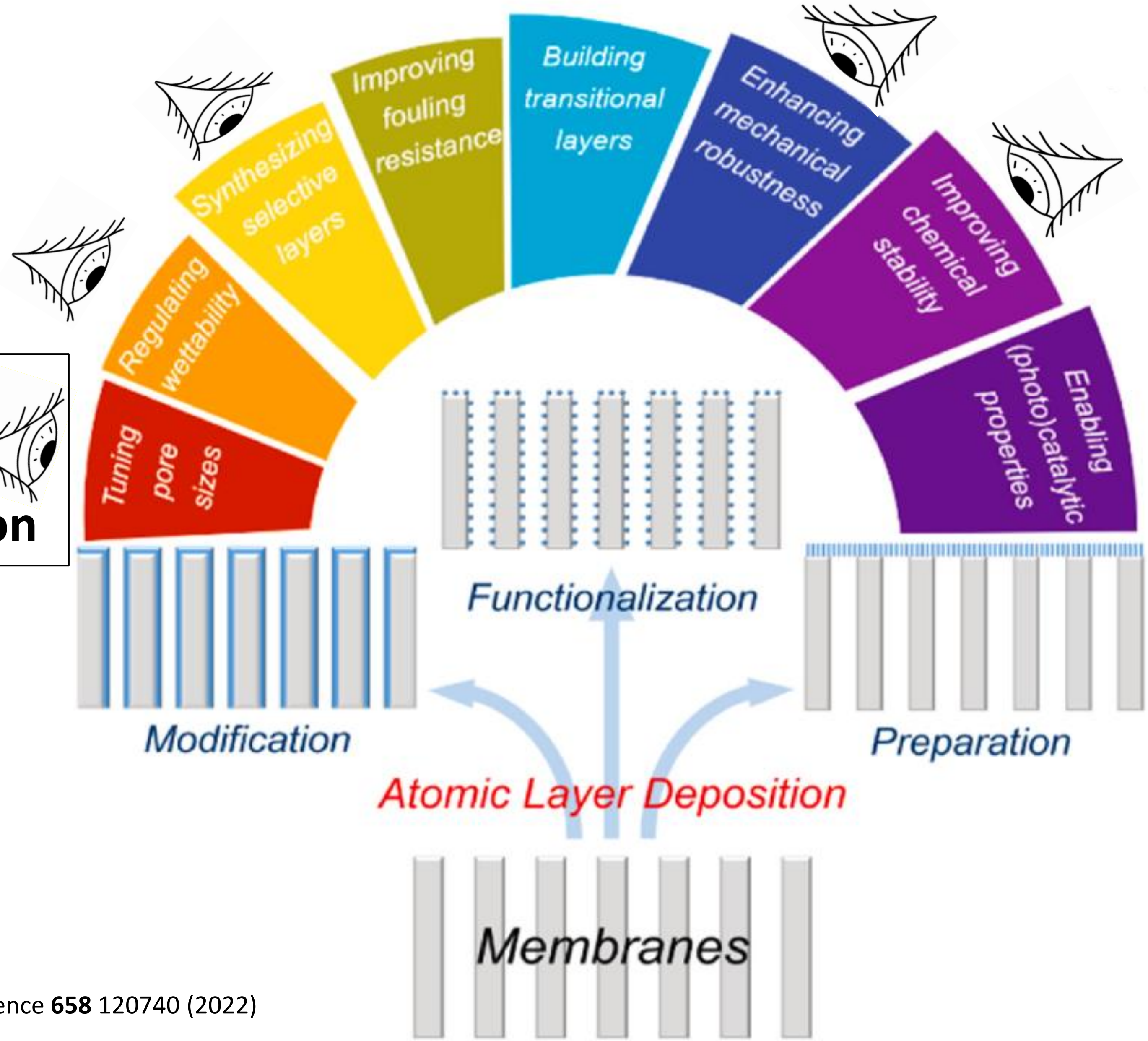
Challenges:

- Pore size, ideally **< 1 nm**
- Narrow pore size distribution for nanofiltration range **< 400 Da**

PFAS: Molecular weight cut-off size: 100 - 1000 Da

Ceramic membranes – many parameters to tune

Focus in this study:
tailor pore size,
pore size distribution

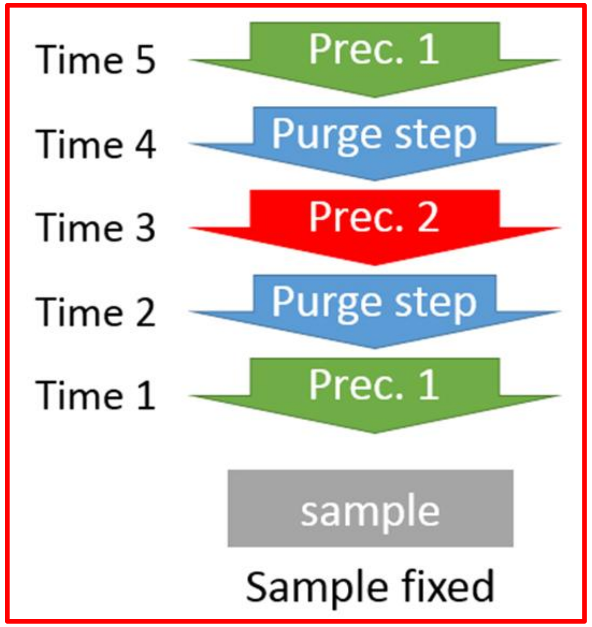


S. Xiong et al., Journal of Membrane Science **658** 120740 (2022)

Atomic-scale deposition: from time- to space-divided

State-of-art Temporal ALD / MLD

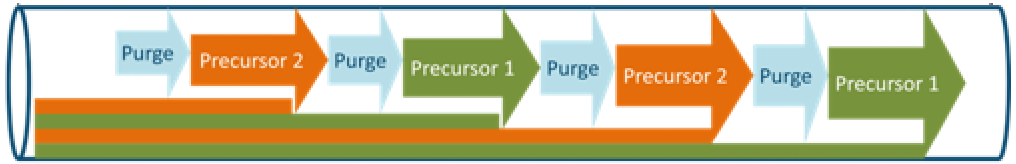
Sequential supply of precursors



Operating at low pressure

Upcoming Spatial ALD / MLD

Constant supply of precursors

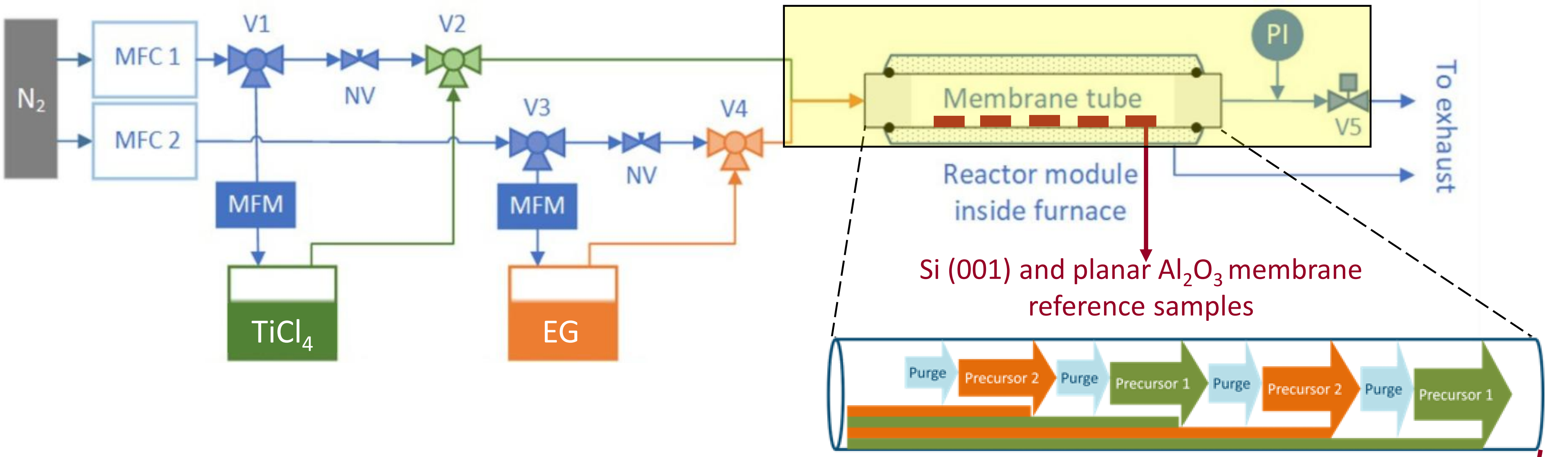


Spatio-temporal ALD

Usually operating at atmospheric pressure

After: D. Muñoz-Rojas

Tubular modular AP-ALD / MLD reactor - home-built at Univ. Twente



Tubular α-Al_2O_3 membrane supports
(1 mm thick, 100 mm long, inner *Φ* 70 mm)

Growth: 450 cycles @125 °C for 20 nm on α-Al_2O_3 (d_{pore}= 20 nm)

Reactant	Pulse time (s)	N_2 purge time (s)	Number of cycles	GPC (nm)
Titanium tetrachloride	1	150	450	0.05
Ethylene glycol	2	150		

Growth Characterization: SE, SEM-EDX, FTIR , XPS

Membrane Characterization:

Permporometry (PPM) → d_{pore} from R_{Kelvin}

Molecular weight cut-off (MWCO) → 90 % of PEG mass retention curve

In-line gas N_2 permeation test → Permeation until pore closure

See also M. Nijboer *et al.*, Separations, **11**, 24 (2024), and back-up slides

Molecular Layer Deposition + post-dep calcination

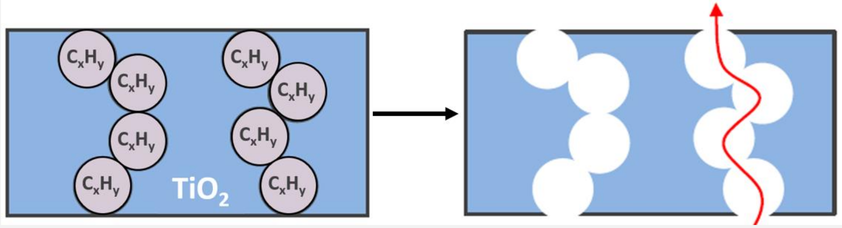
Basics:

2 ╟OH + $TiCl_4$ → ╠O_2-Ti-Cl_2 + 2 HCl

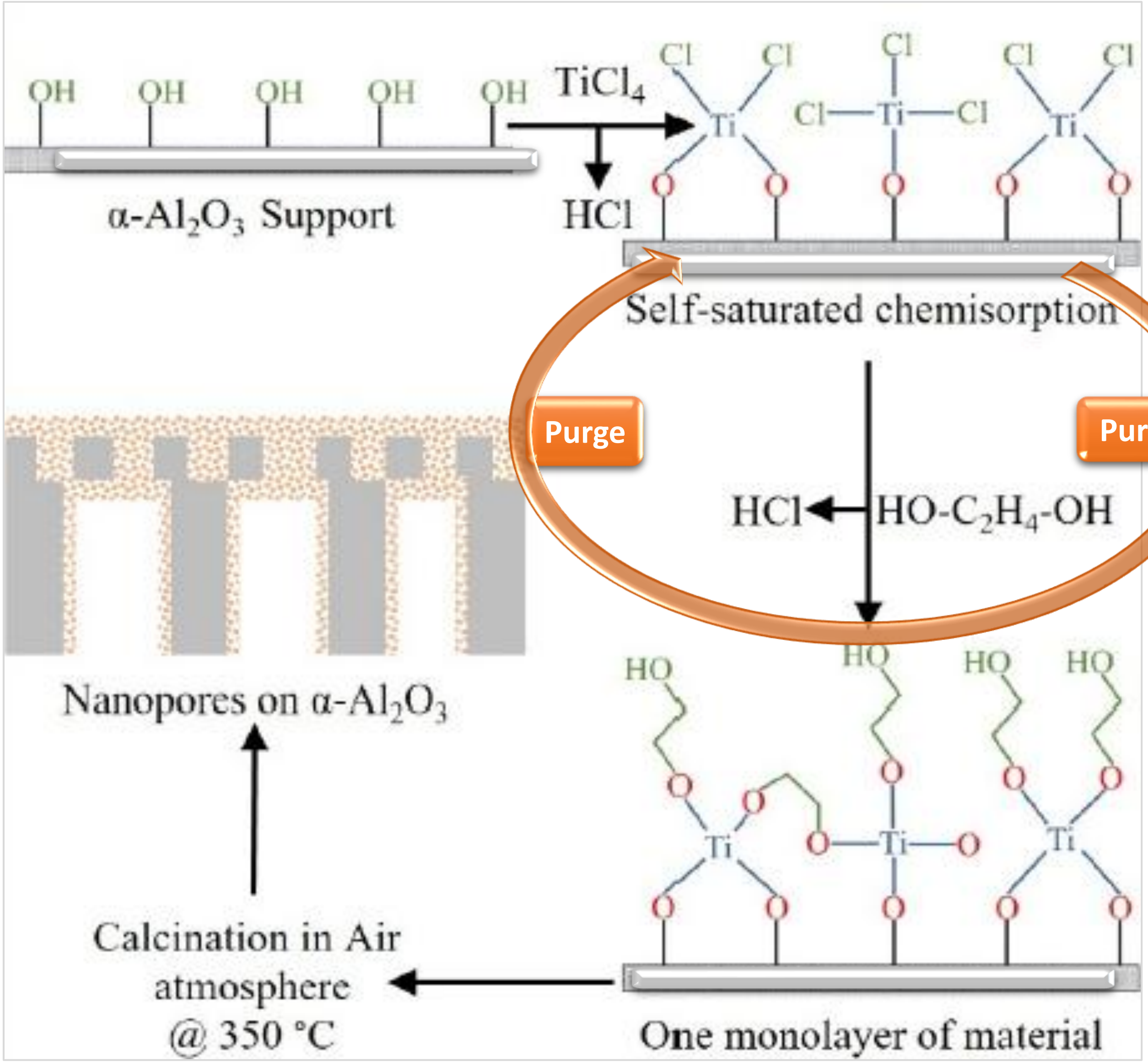
╟O-$TiCl_3$ + $C_2H_6O_2$ → ╠O-Ti-$C_2H_3O_2$ + 3 HCl

╟ monodentate, ╠ bi-dentate adsorption

- C_xH_y groups embedded in TiO_2 matrix
- Calcination to create porous network
  → MLD yielding titanicone as ***porogen***



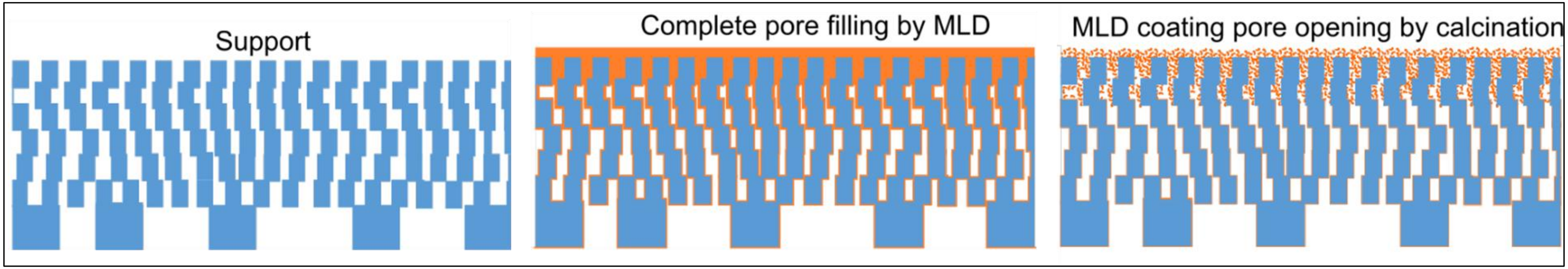
- Vary organic C_xH_y groups to tune pore size, and functionalize hydrophobicity, etc. (aliphatics, aromatics, ..)

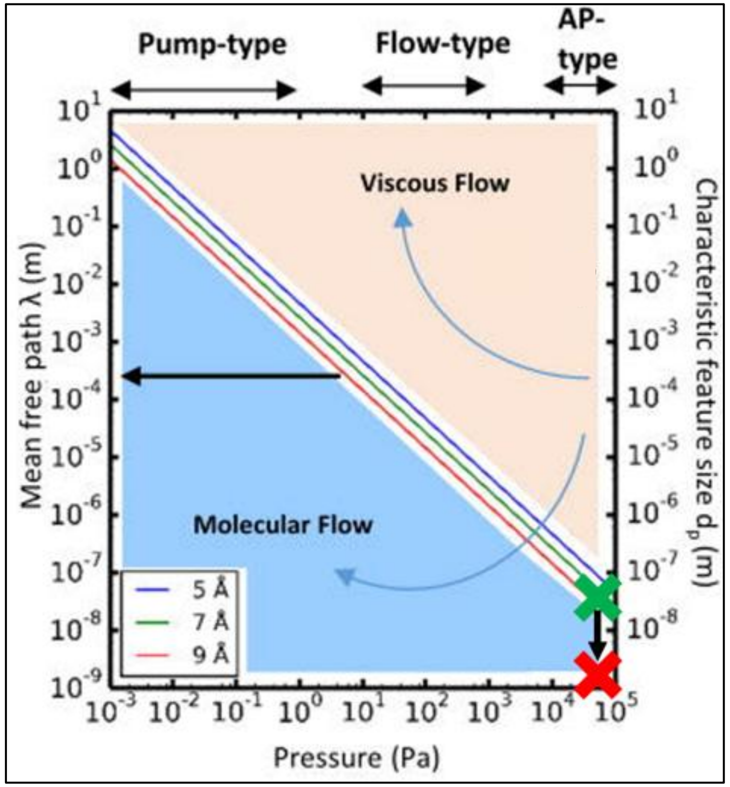


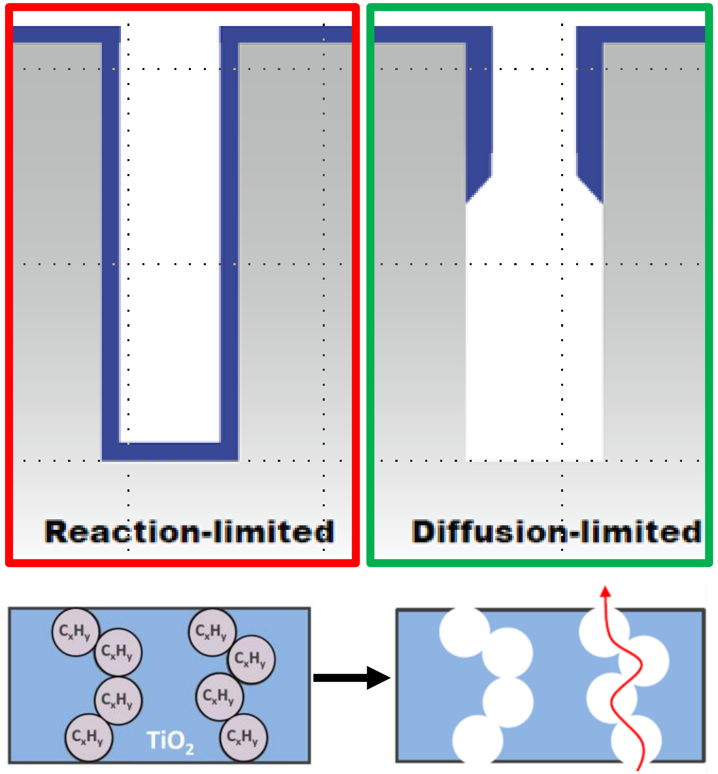
H. Sondhi, et al., Membranes, **15**(3) 86 (2025)

Molecular Layer Deposition + post-dep calcination

Basics: filling of a mesoporous support with an initial average pore size of 20 nm

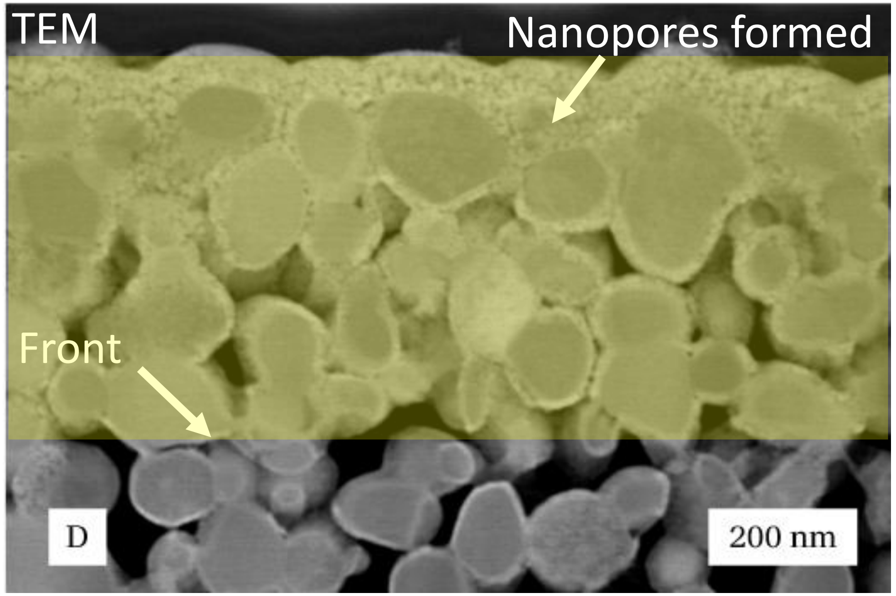






→ Diffusion-limited

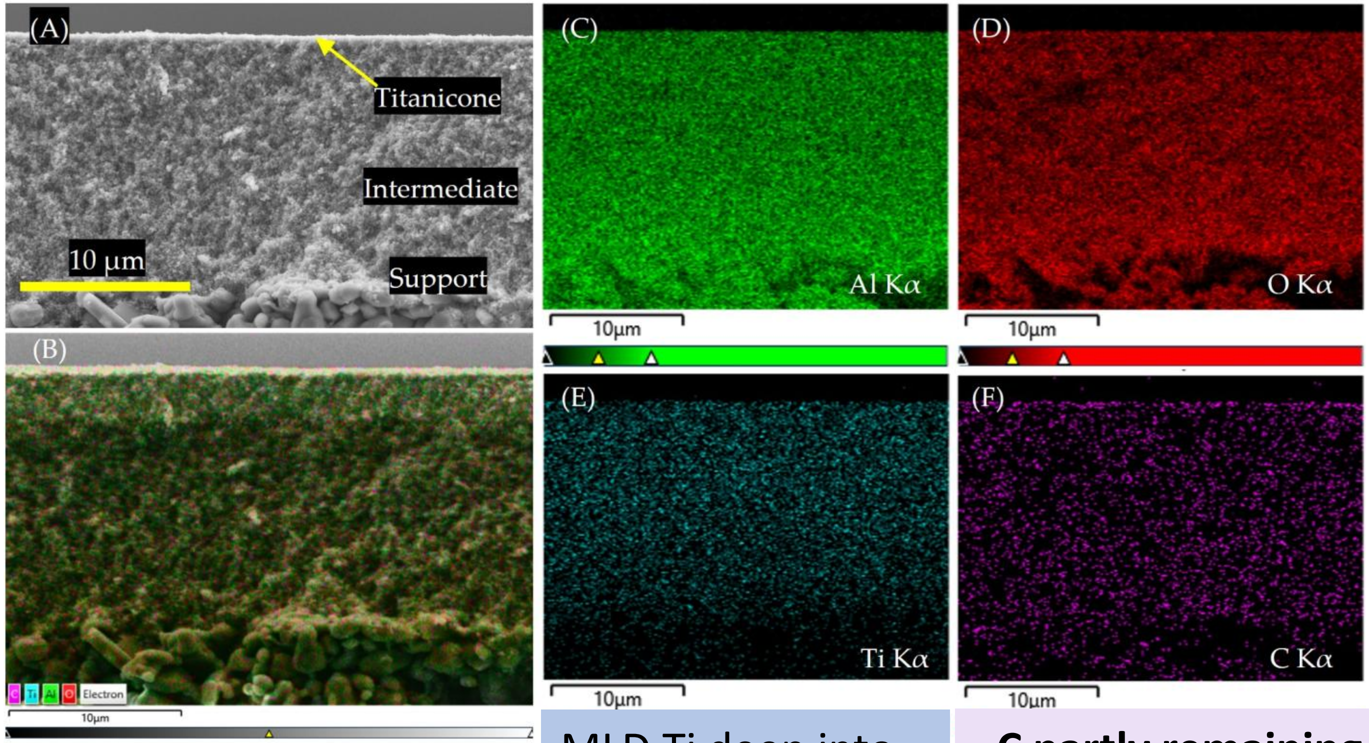
Downwards moving saturation front ↓



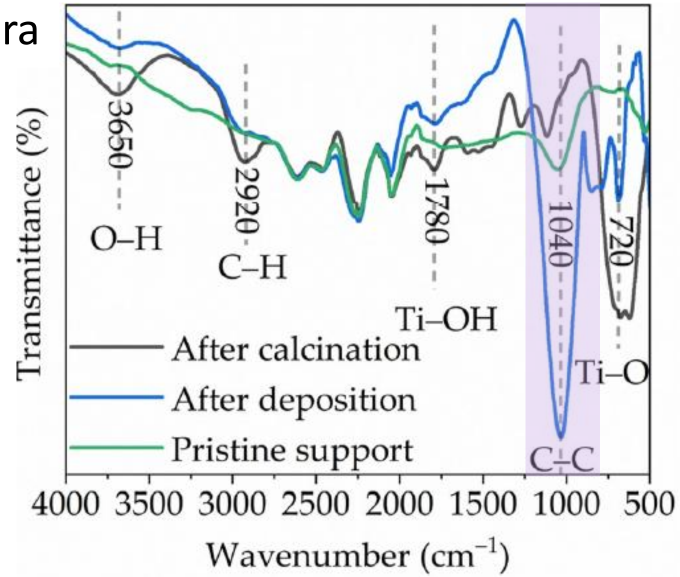
Molecular Layer Deposition + post-dep calcination

20 nm thick $TiCl_4$-EG titanicone layer grown on tubular α-Al_2O_3 substrate and annealed at 350 °C

Cross-section SEM - EDX mappings

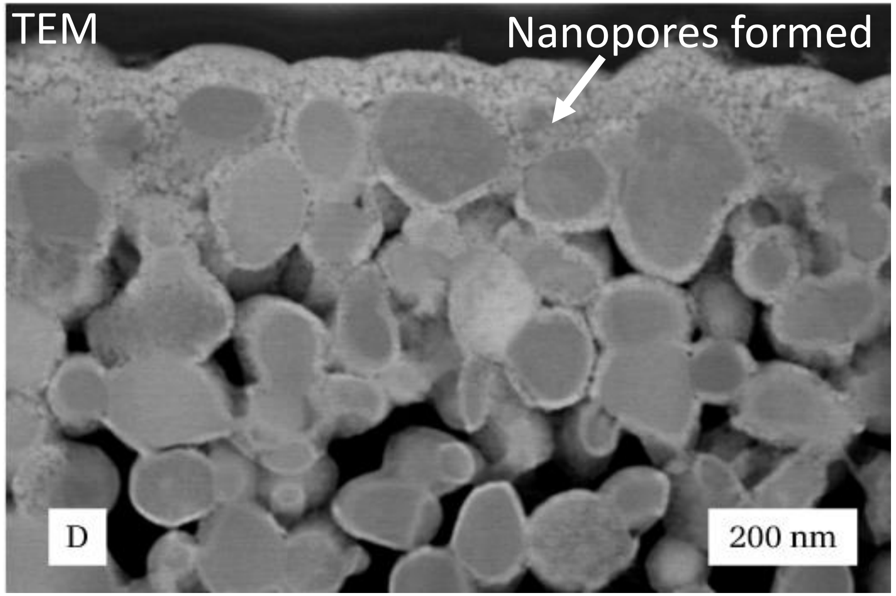


FTIR spectra



MLD Ti deep into tubular α-Al_2O_3 support

C partly remaining
→ parameter to functionalize *hydrophobocity*

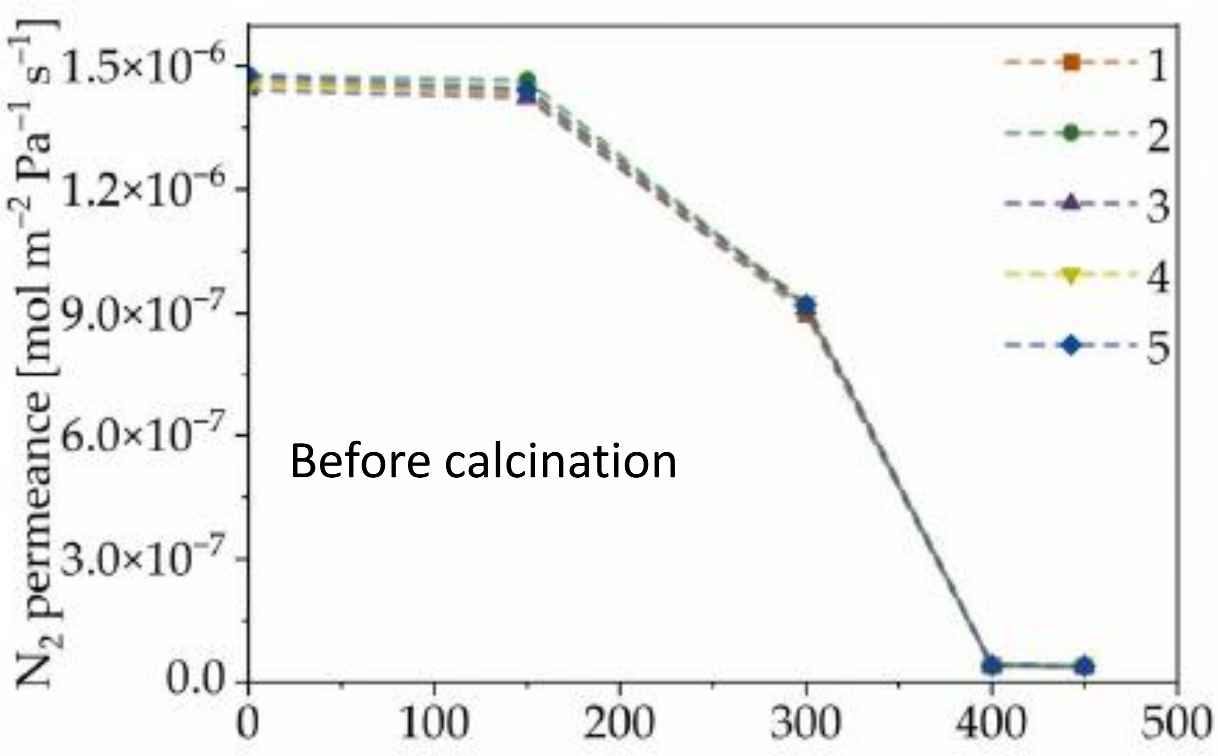


H. Sondhi, et al., Membranes, **15**(3) 86 (2025)

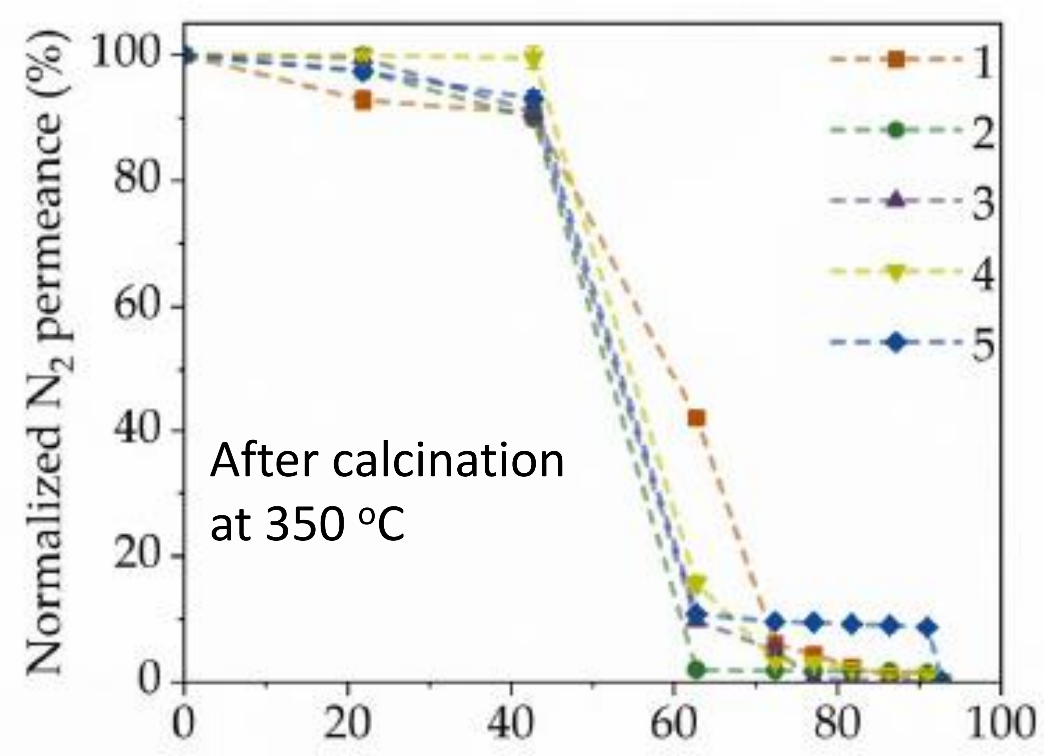
Molecular Layer Deposition + post-dep calcination

20 nm thick $TiCl_4$-EG titanicone layer grown on tubular α-Al_2O_3 substrate and annealed at 350 °C

N_2 permeance measurements of 5 identically grown membranes



Number of MLD cycles



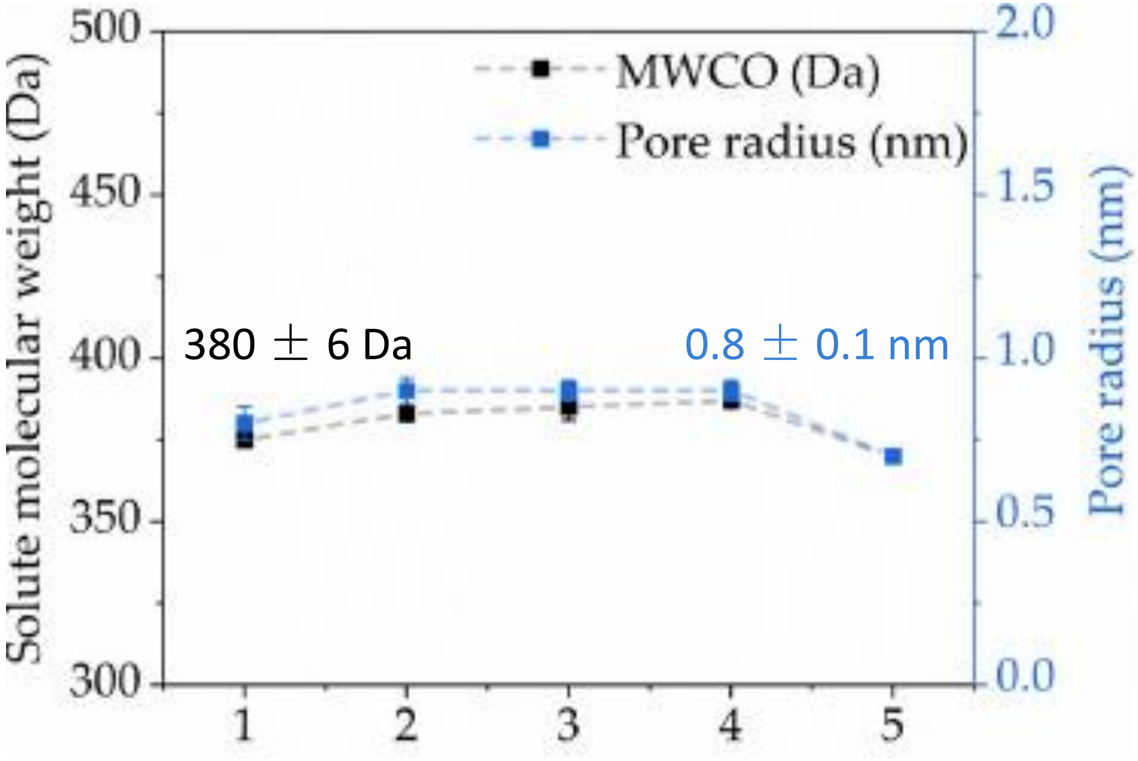
Relative partial pressure (p/p_s)
normalized as f ($p_{water\ vapor}$)

H. Sondhi, et al., Membranes, **15**(3) 86 (2025)

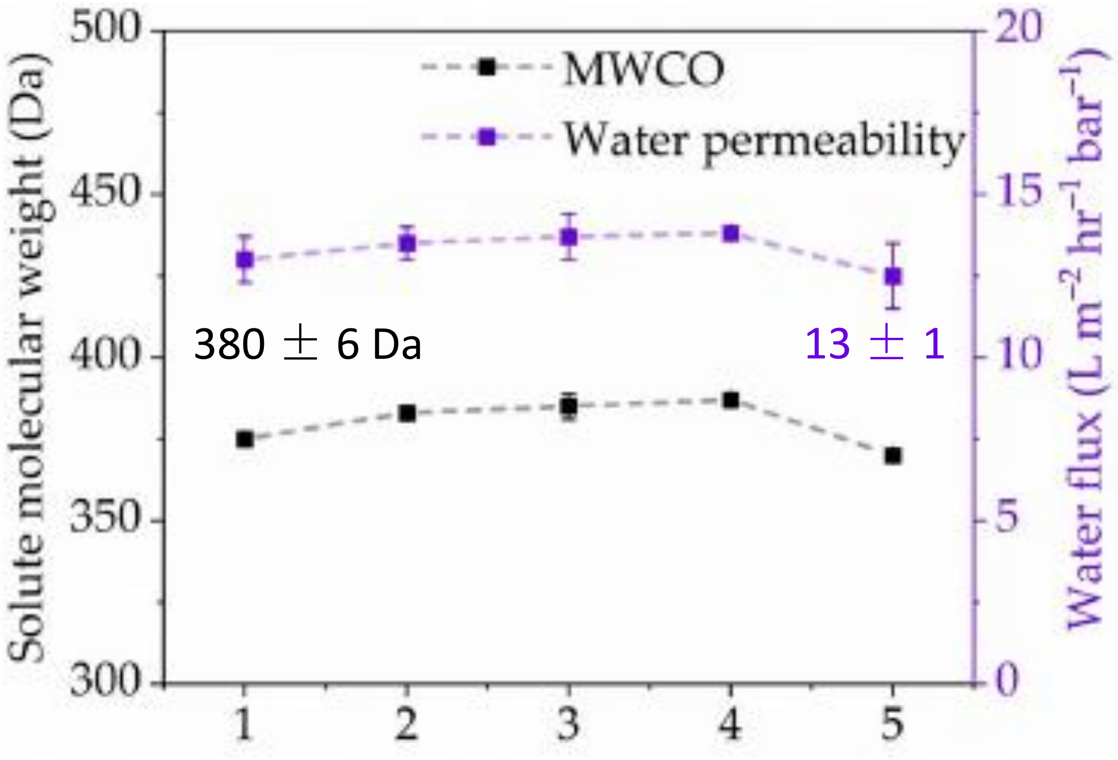
Molecular Layer Deposition + post-dep calcination

20 nm thick $TiCl_4$-EG titanicone layer grown on tubular α-Al_2O_3 substrate and annealed at 350 °C

MWCO measurements at 20 °C of 5 identically grown membranes



Sample number



Sample number

H. Sondhi, et al., Membranes, **15**(3) 86 (2025)

Filtration characteristics

Commercial polymeric membrane NF200 vs. calcined titanicone hybrid layer membrane on α-Al_2O_3

Membrane Type	Temperature (°C)	Pressure (bar)	MWCO (Da)	Water flux ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)
NF200 *	20	20	300–360	7.7
	25	20	-	8.65
	30	20	-	9.71
Calcined titanicone hybrid layer	20	9	380 ± 6	13 ± 1
	25	9	-	19 ± 0.7
	30	9	-	21 ± 0.5

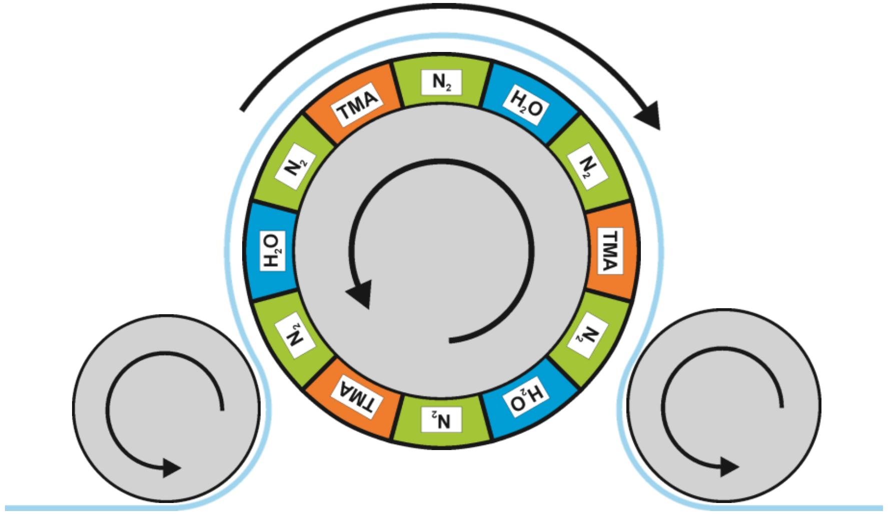
* A.A. Merdaw, et al., Desalination **260**, 190 (2010)

~2x higher water permeability at ~2x lower operational pressures

H. Sondhi, et al., Membranes, **15**(3) 86 (2025)

Outlook: many other parameters to tune, incl. polymers

Non-swelling top layer on polymeric membranes with SALD (sheet-to-sheet, or roll-to-roll) ?



- Center piece: Foil surrounding a drum with multiple reaction zones and N_2 gas-bearings
- Foil moves clockwise (slowly)
- Fast multi-nozzle ALD injector rotates CCW

- **No mechanical contact on deposition side**
- **Flexibility in foil and layer thickness**
- **Compact**

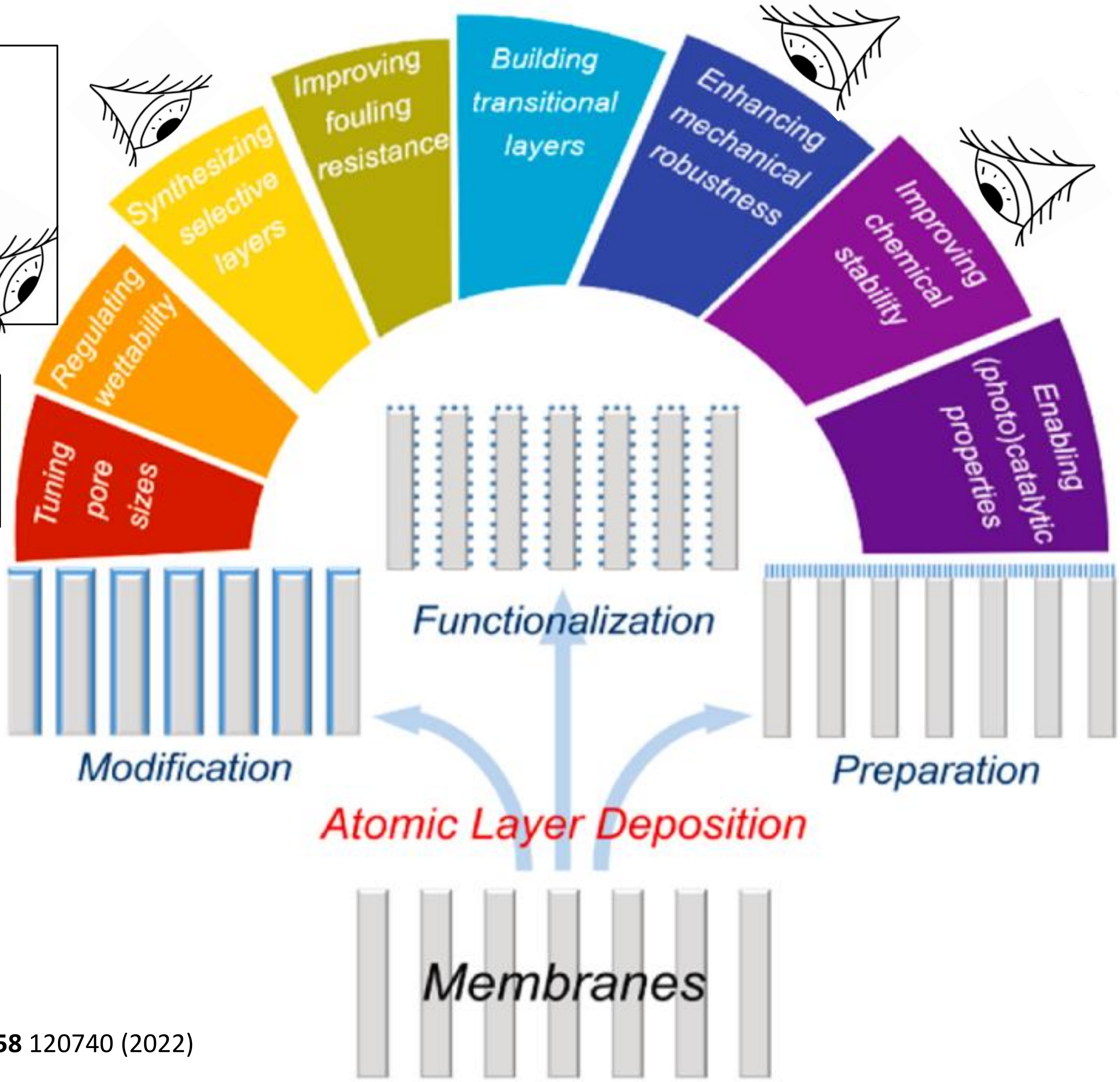
- P. Poodt. D. Cameron, E. Dickey, S.M. George, V. Kuznetsov, G.N. Parsons, F. Roozeboom, G. Sundaram, A. Vermeer, JVST-A **30** (2012) 10802

- Patented by TNO, Netherlands

Outlook: many more parameters to tune

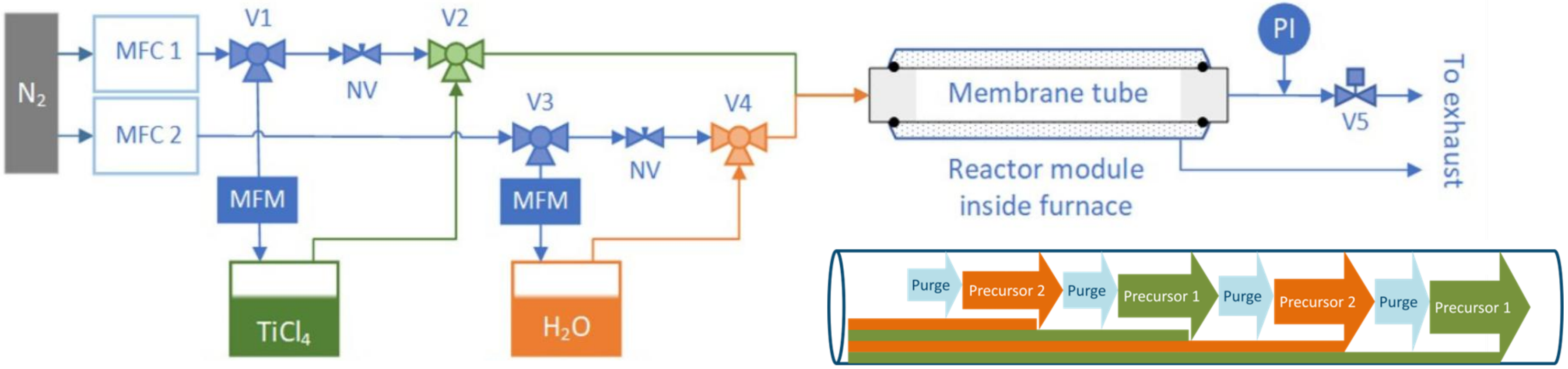
Hydrophobicity as a function of
-annealing ambient
-annealing temperature
-organic co-reactant

This study: pore size



S. Xiong et al., Journal of Membrane Science **658** 120740 (2022)

Concluding remarks



- Ceramic nanofiltration membranes made from MLD-grown titanicone (as porogen layer) and subsequent annealing at 350 °C

- Layer growth & pore closure monitored with *inline* pressure test

- Sharp cut-off at MWCO <380 ± 6 Da

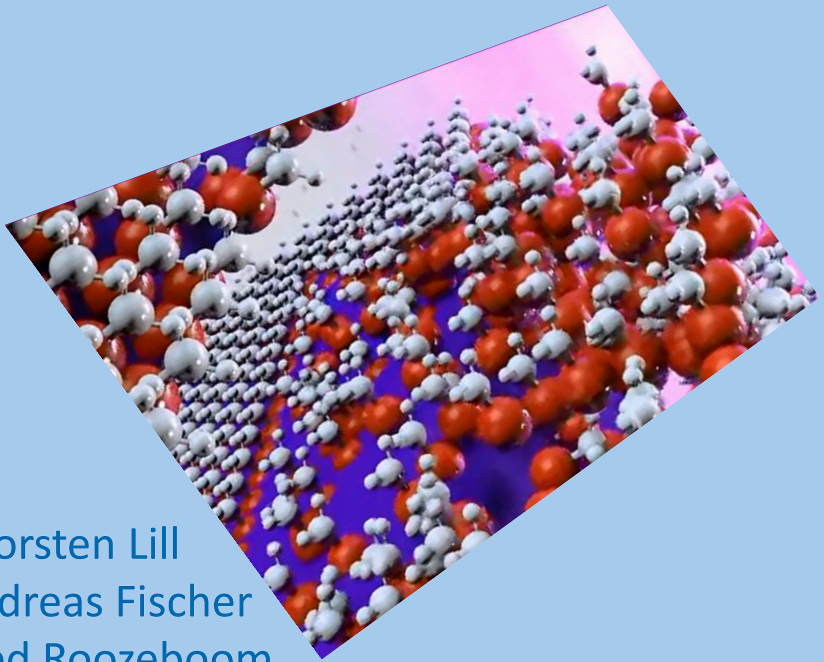
- Compared to polymeric commercial NF200 membrane:
  ~**2x** higher water permeability (~13 ± 1 $L.m^{-2}.h^{-1}.bar^{-1}$)) at ~**2x** lower operational pressure (9 bar)

- Hydrophobicity control by organic co-reactant plus post-dep calcination in N_2 (or other) atmosphere

Thank you for listening

Announcement: Appearing soon (late 2025)

Atomic Layer Processing: Applications in Advanced Semiconductor Devices



Thorsten Lill
Andreas Fischer
Fred Roozeboom

SPIE.

Society of Photo-Optical Instrumentation Engineers

T. Lill, A. Fischer and F. Roozeboom, *Atomic Layer Processing: Applications in Advanced Semiconductor Devices*, SPIE Press, Society of Photo-Optical Instrumentation Engineers, Bellingham (WA), USA, 2025 (in press, ~**250 pages**)

Note: cover is not final

Back-up slides

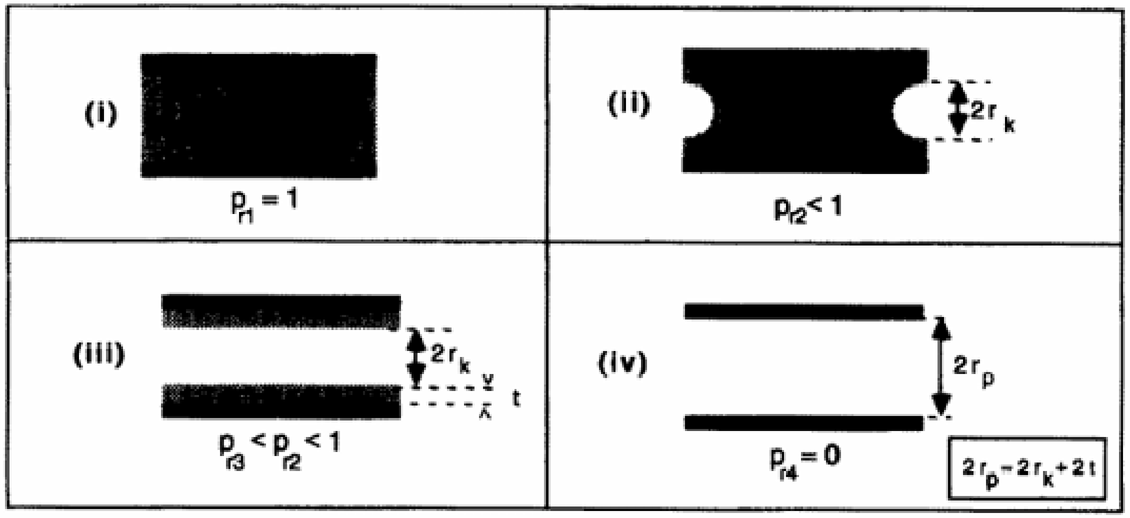
• Permporometry (PPM)

Nitrogen flux through a membrane while increasing the water partial pressure in steps from 0 to 90 % RH

Water capillary condensation inside the pores → Decrease in nitrogen flux

→ $d_{pore} = R_{Kelvin} + 2 \times t_{layer\ thickness}$ (Kelvin equation)

F.P. Cuperus et al./J. Membrane Sci. 71 (1992) 57–67



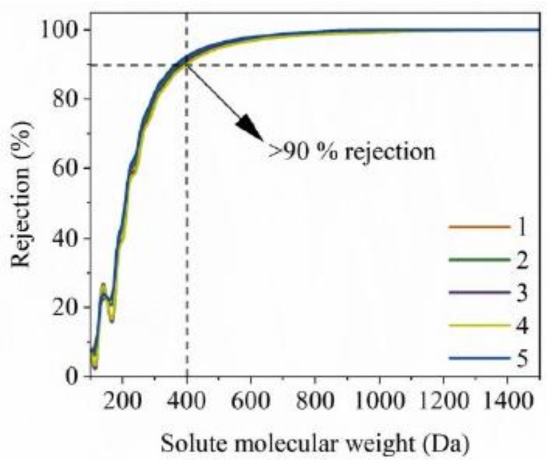
Steps in the **desorption** process:
(i) liquid filled pore, at saturation pressure,
(ii) just before desorption starts, pore is still filled
(iii) just after evaporation is complete, t-layer remains
(iv) after complete desorption

See also:
M. Nijboer *et al.*, Separations, **11**, 24 (2024)

Membrane characterization (2)

• Molecular weight cut-off (MWCO)

Mixture of polyethylene glycol (PEG) solution (1 g L^{-1}) with mean molecular weights of 200, 400, 600, 1000, and 1500 g mol^{-1} is filtered by the membrane at 10 bar pressure. Afterward, samples from the feed, permeate, and retentate are measured
→ MWCO of membrane determined at the x-axis intercept of 90 % of the retention curve



• *In-line* gas N_2 permeation test to follow the progress of ALD/MLD layer deposition in the pores until pore closure :

In between a pre-determined number of growth cycles, a permeation test is done using flows of 20 and 50 $ml.min^{-1}$.
The N_2 flow is set to be constant, and the pressure drop over the membrane is read from the digital backpressure regulator.
The pressure drop value is converted into a N_2 permeance *P* using:

$$P = F / (6 \times 10^9 \times a \times \Delta p \times V_m)$$

where *P* is the permeance in [$mol.m^{-2}.Pa^{-1}.s^{-1}$], *F* the flow of nitrogen in $ml.min^{-1}$, *a* is the tubular membrane surface area in m^2, and Δp the pressure difference in bar, and V_m the molar volume of N_2 at atmospheric pressure and room temperature

See also:
M. Nijboer *et al.*, Separations, **11**, 24 (2024)