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Membrane-assisted Ethylene Synthesis over
Nanostructured Tandem Catalysts

Advancements in Carbon-Based Membrane Development: From Design to Applications

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Sustainable Energy &
Process Technologies

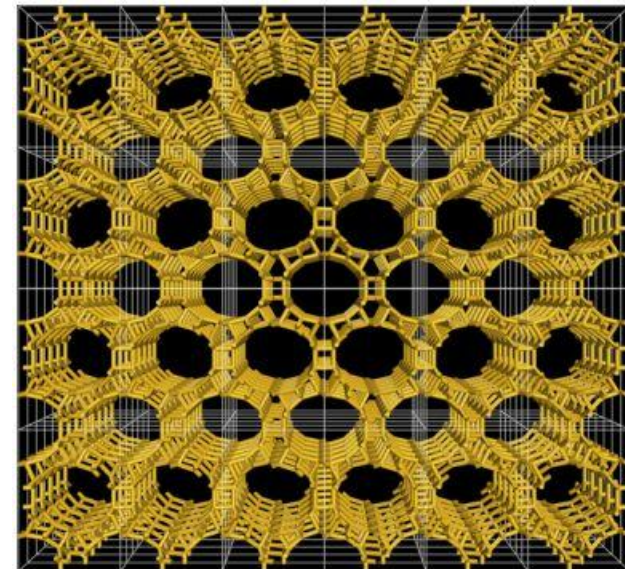
Eindhoven, 21th-23rd Oct. 2025

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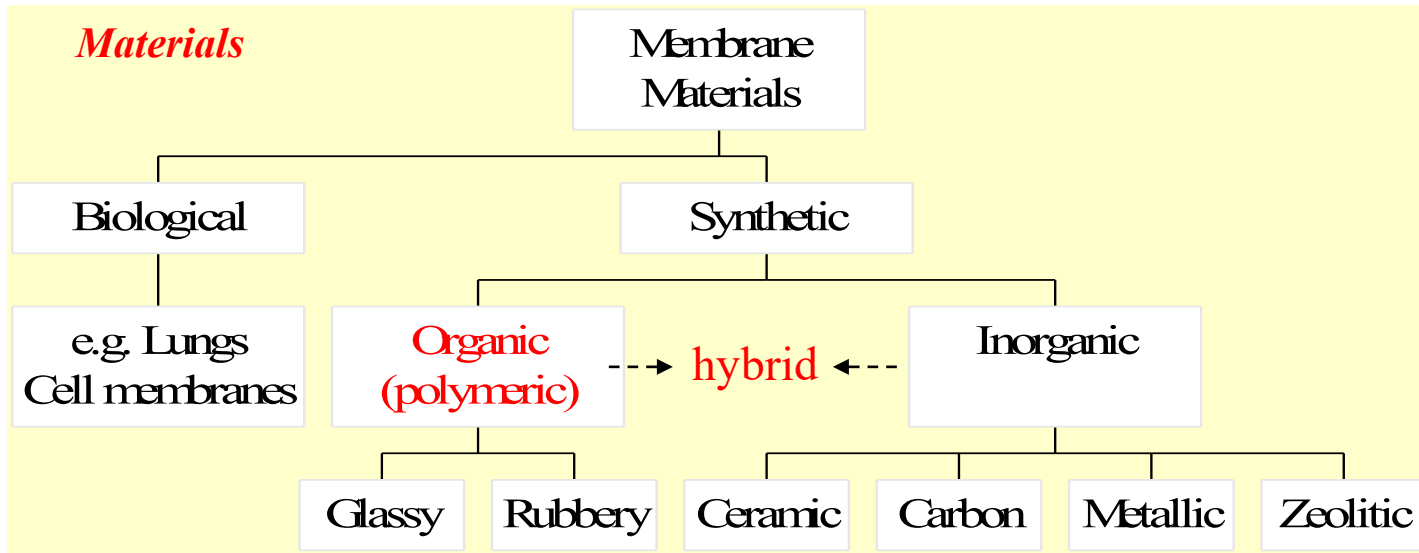
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Outline

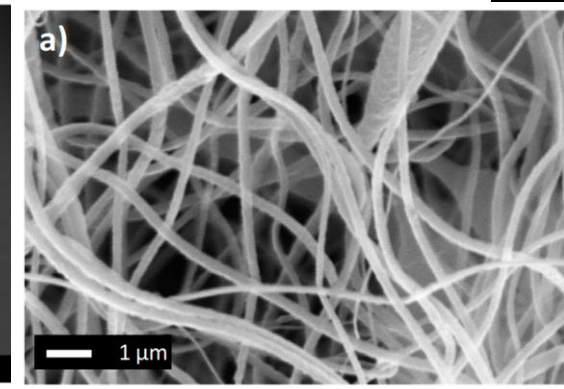
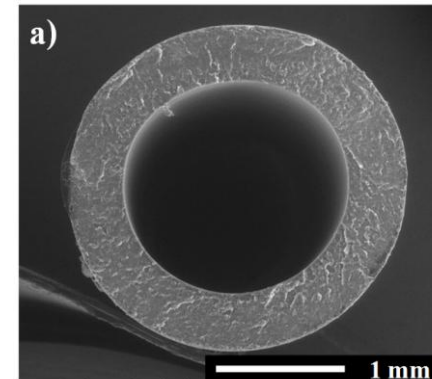
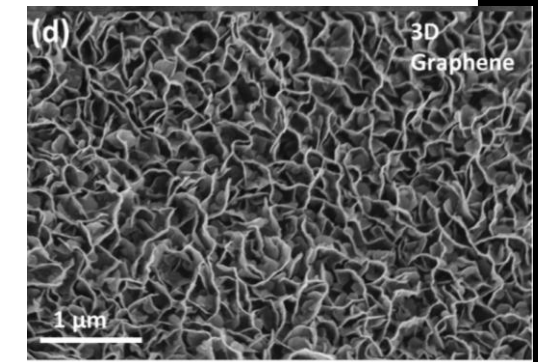
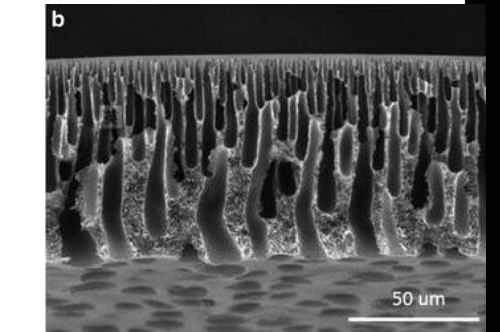
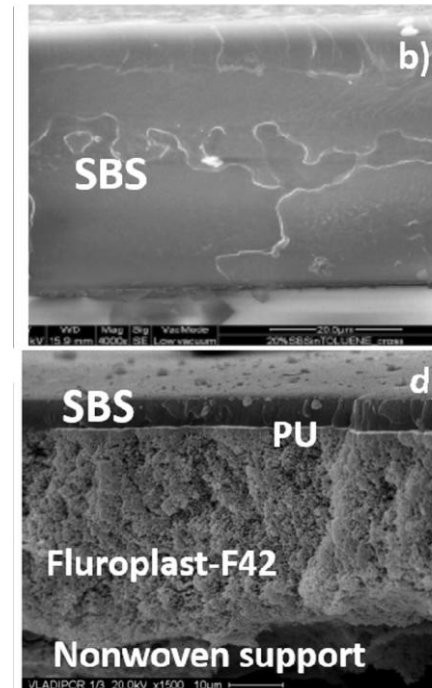
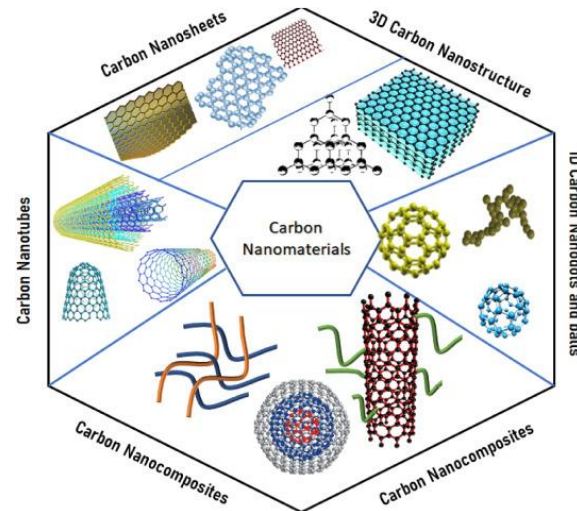
- ❖ Introduction: Carbon & Membranes
- ❖ Carbon-doped membranes: towards sustainable and energy-efficient desalination
- ❖ Carbon molecular sieve membranes: applications in membrane reactors



Membranes & Carbon

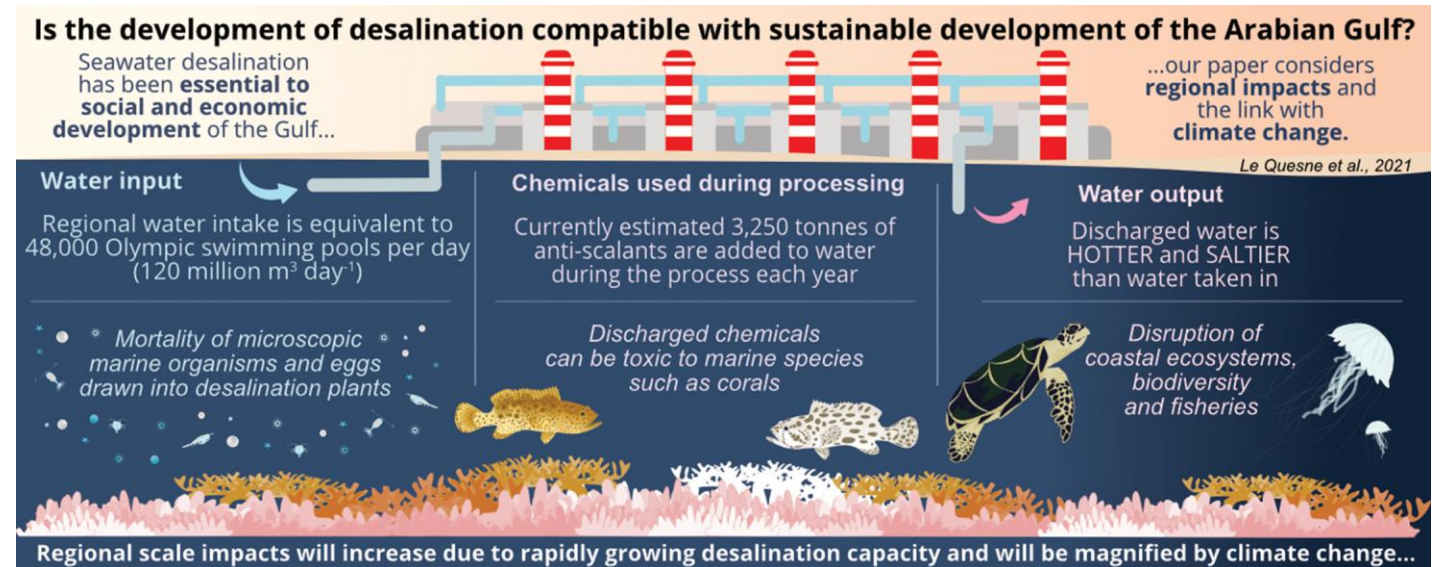


Carbon nanomaterials are often employed to produce hybrid membranes, imparting functional properties such as enhanced selectivity, antifouling behavior, or photothermal response to conventional polymeric membranes.



Reverse Osmosis: The Success Story of Membrane Technology

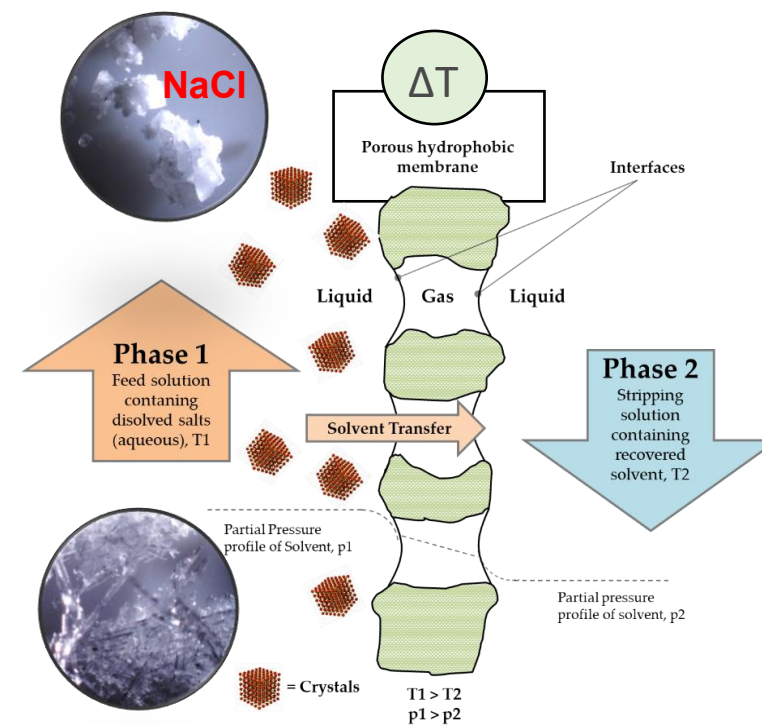
- ❖ Removal of 95-99% of dissolved salts
- ❖ Advantageous with respect to thermal desalination
- ❖ Poor feasibility for salinity > 65,000 mg/L
- ❖ Relatively low water recovery factor (50%)
- ❖ Environmental impact related to the huge volume of brine discharged from SWRO



SWRO requires an urgent paradigm shift towards environmental sustainability by implementing circular economy approaches for brine valorization

Membrane Distillation-Crystallization

- ❖ MD requires MICROPOROUS HYDROPHOBIC MEMBRANES
- ❖ The operation is driven under a moderate gradient of vapor pressure, often induced by a TEMPERATURE GRADIENT
- ❖ Because of the low sensitivity to osmotic phenomenon, high concentration factors can be reached (up to 90%)
- ❖ The extension of MD practices up to the supersaturation of the retentate, named MCr, enables the heterogeneous nucleation of solutes and the growth of crystals



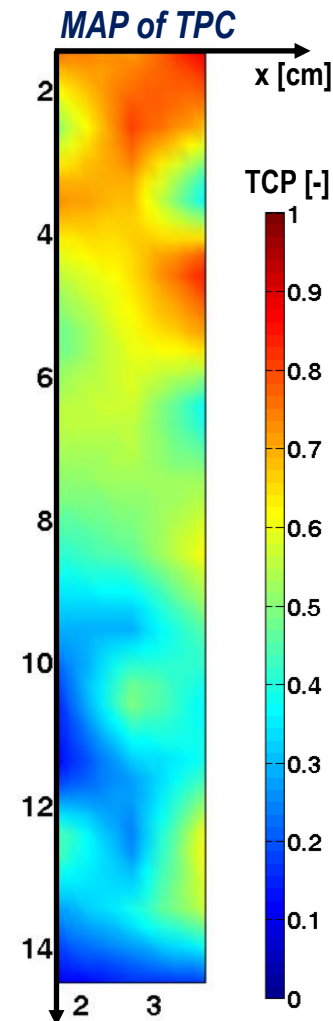
$$J_w = K \left(p_w^{feed} - p_w^{distillate} \right)$$

MD-MCr has the potential to intensify the desalination industry and valorizing the SWRO brine by: i) improving the water recovery factor and ii) extracting minerals.

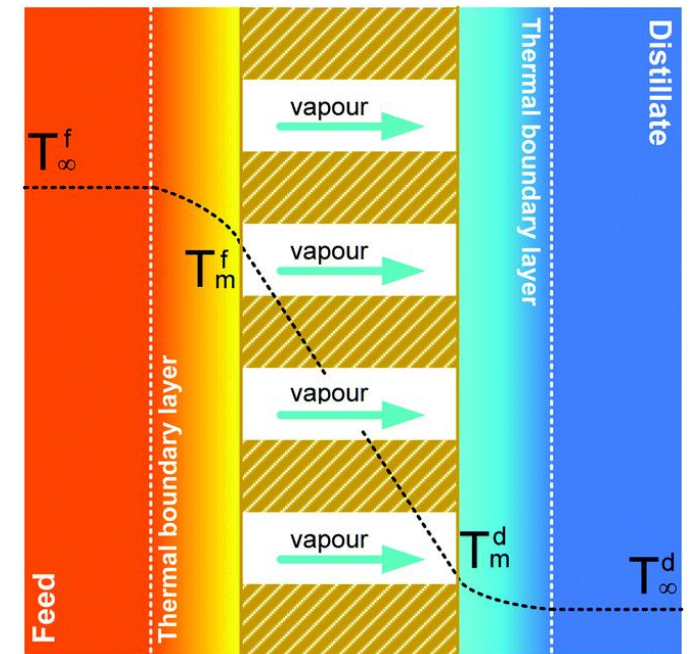
Temperature Polarization

- ❖ Temperature polarization (TP) is mostly related to the removal of latent heat associated with water evaporation
- ❖ Because TP, the overall efficiency of the MD-MCr process drastically falls (<50%)
- ❖ Hybridization of MD-MCr with solar energy secure the production of with a specific energy consumption of 200–300 kW h m⁻³
- ❖ TP is quantified by the temperature polarization coefficient (TPC):

$$TPC = \frac{T_m^f - T_m^d}{T_\infty^f - T_\infty^d}$$



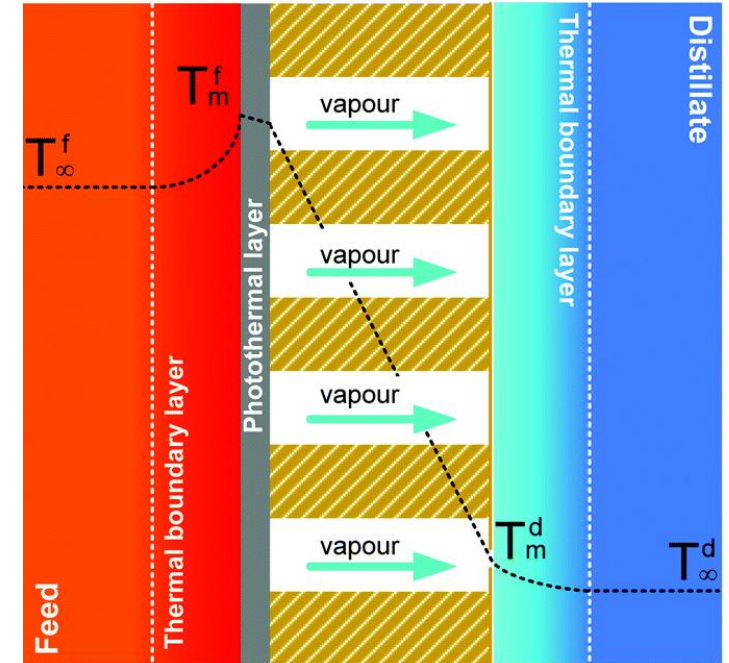
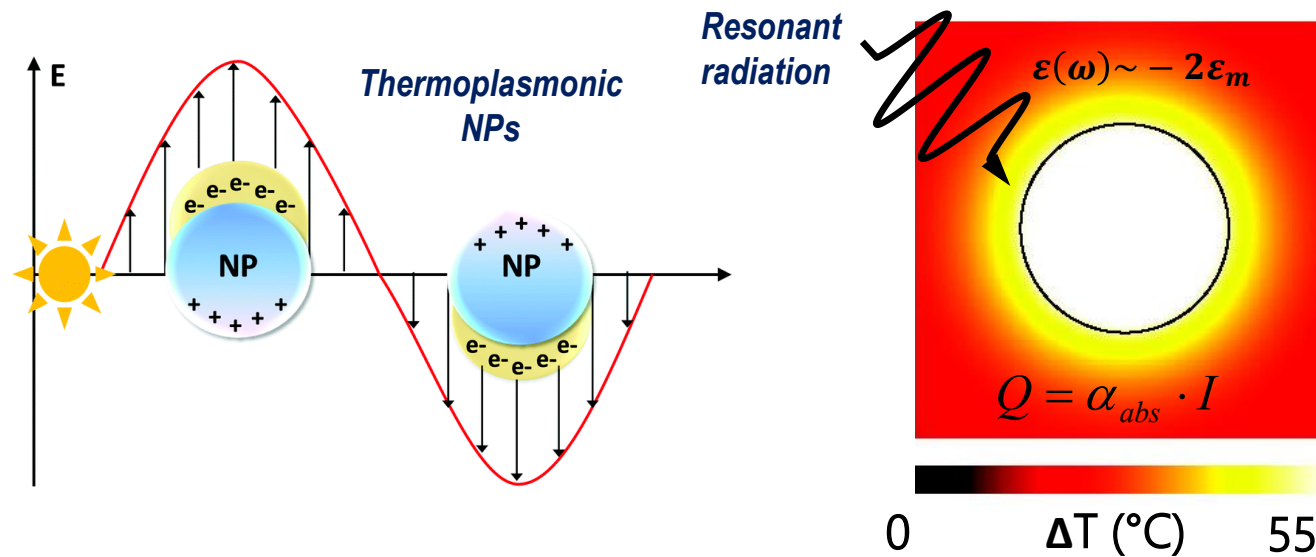
Direct Contact Membrane Distillation (DCMD)



How to mitigate TP?

The advent of Photothermal MD

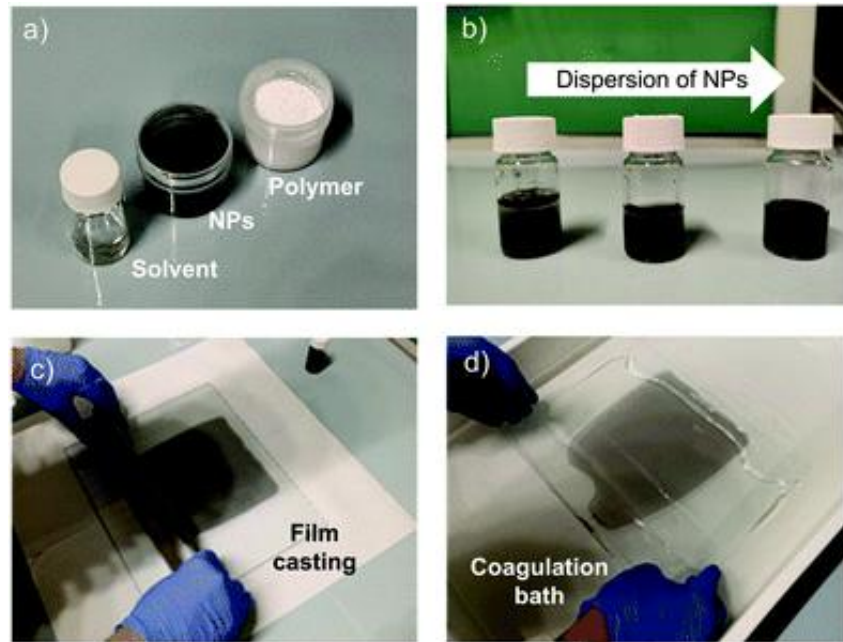
- ❖ Plasmonic Nanoparticles (NPs), such as Au or Ag, guarantee high light-to-heat conversion



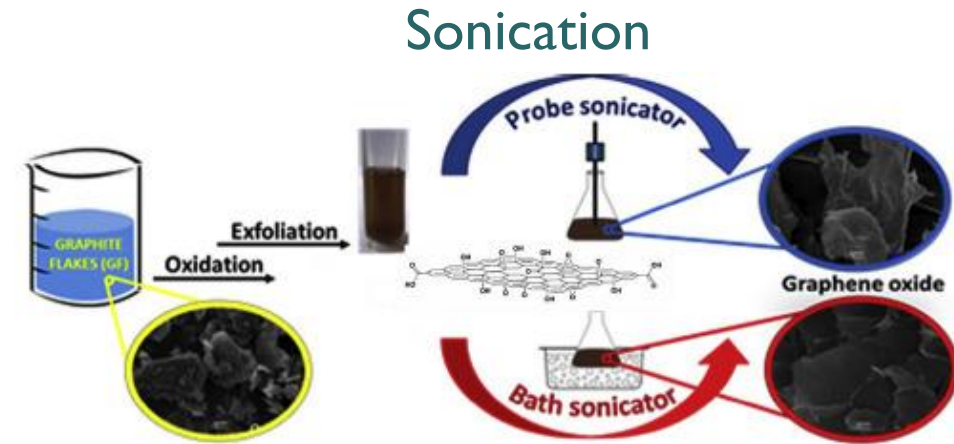
- ❖ Their immobilization on MD membranes enables the development of self-heating membranes ensuring a light-driven desalination

Photothermal MD overcome the bottleneck of the process

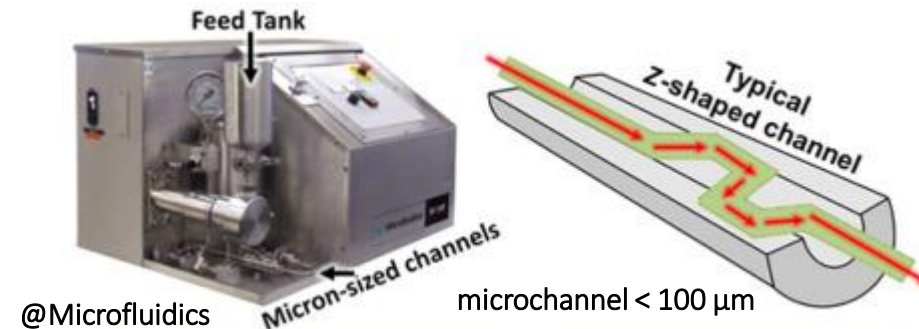
Membrane preparation via non-solvent induced phase separation (NIPS)



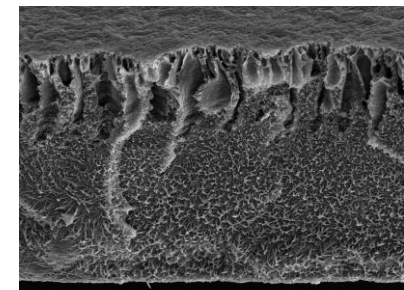
Preparation of homogeneous membranes via non-solvent induced phase separation (NIPS): (a) materials, (b) preparation of the polymeric solution, (c) casting of the polymeric solution, (d) NIPS induced by the coagulation bath.



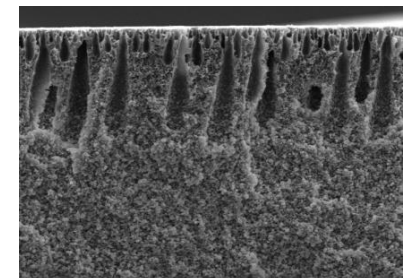
Liquid-Phase Exfoliation (LPE)
Pressure: 210 MPa (shear rate 10^6 s^{-1})



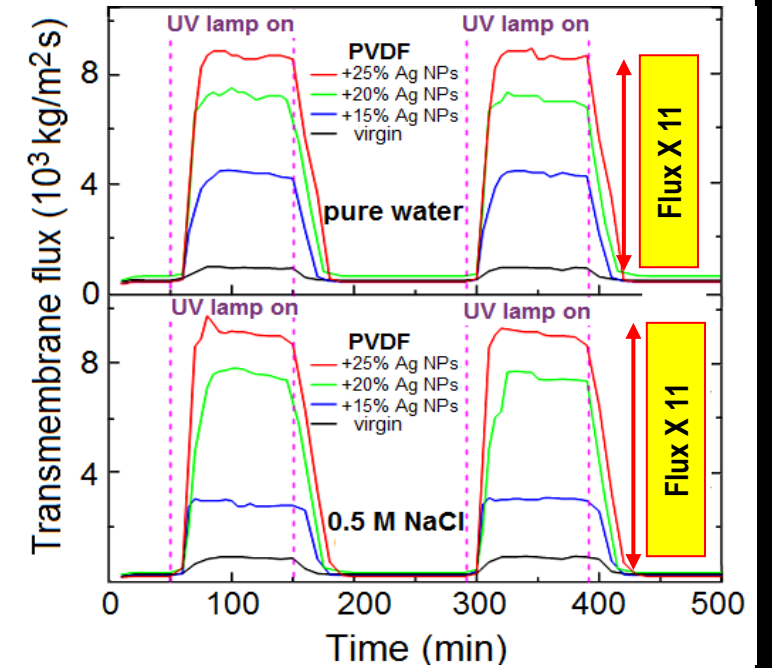
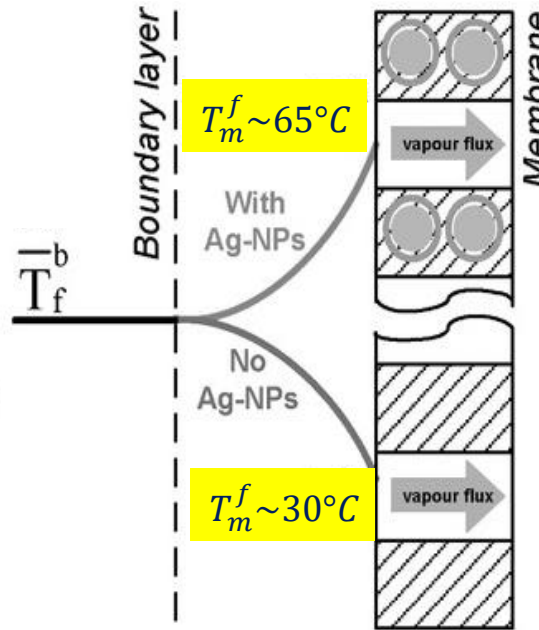
PhMD based on Silver Nanoparticles (Ag NPs)



PVDF membrane, 20% AgNPs

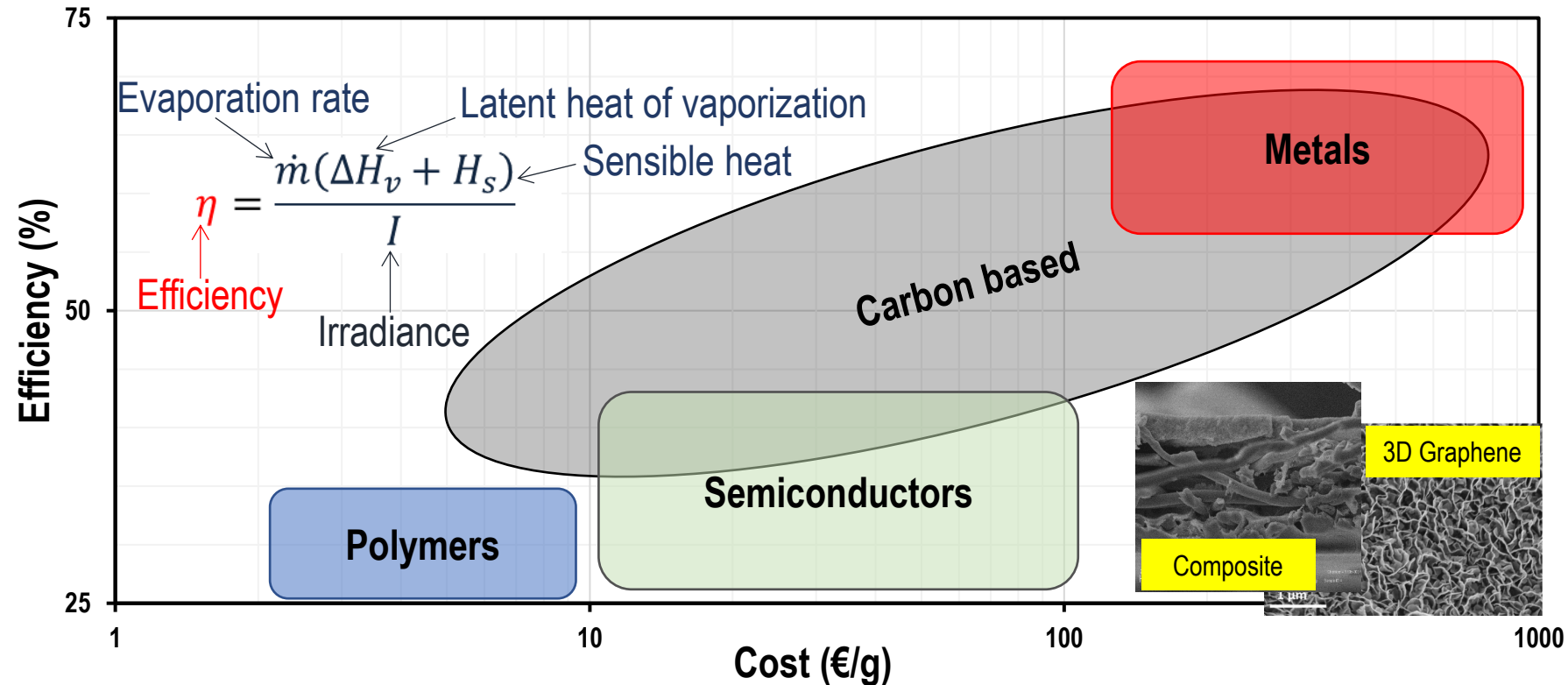


PVDF membrane, 25% AgNPs



The high cost of the membranes and the employment of the UV radiation hampered the practical implementation of Ag-based photothermal mixed matrix membranes

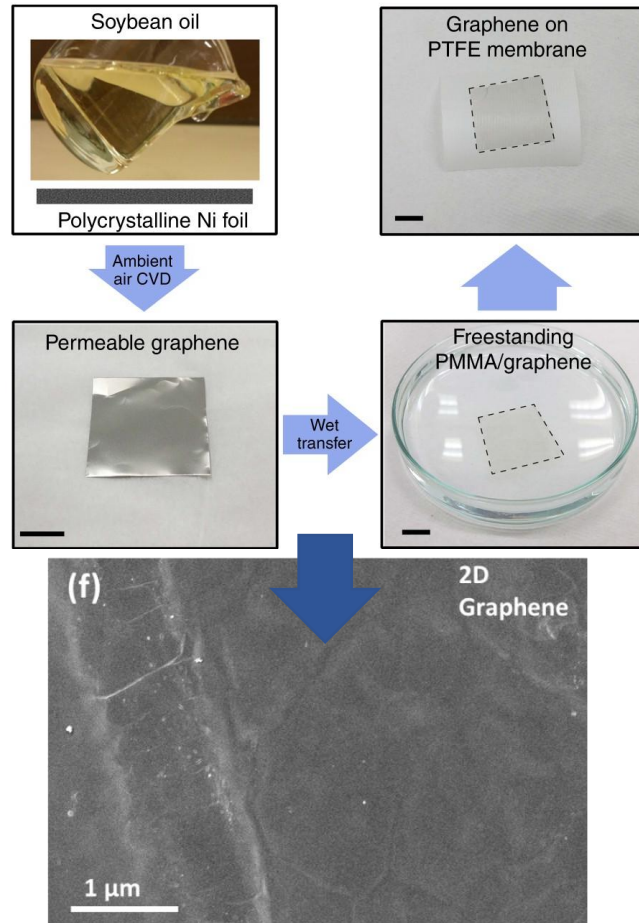
Development of photothermal membranes



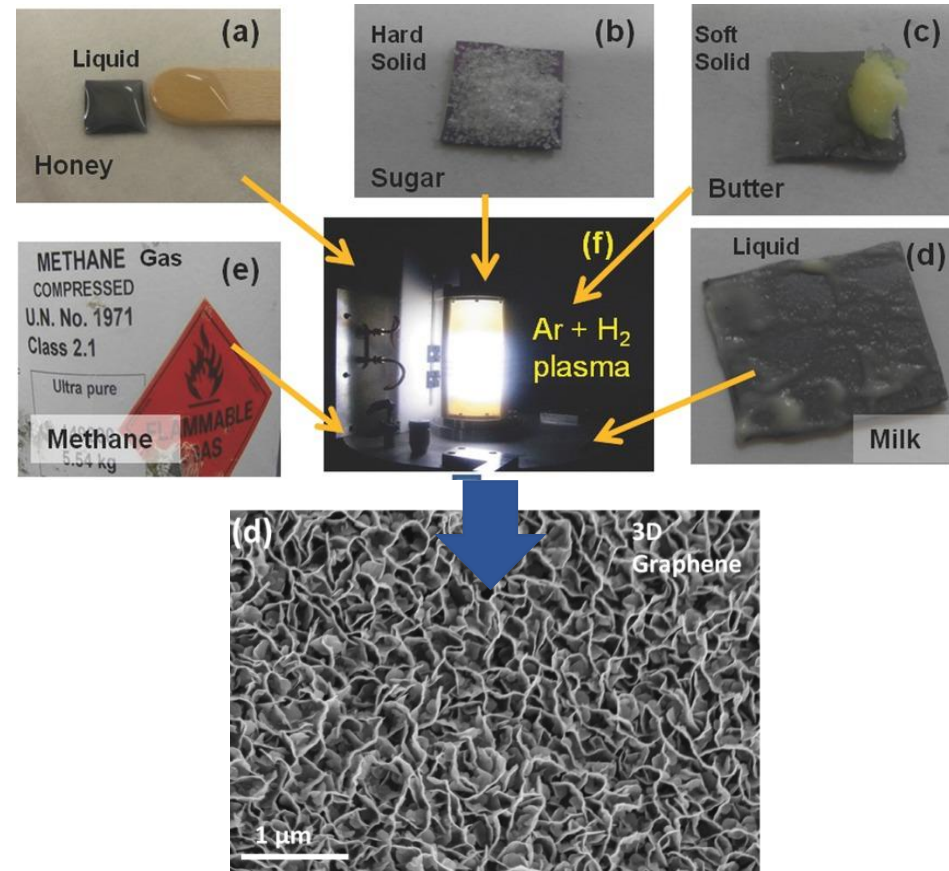
- ❖ Composite membranes to reduce the cost of the membrane and localize the light-to-heat conversion on membrane surface
- ❖ Development of photothermal membranes able to exploit the solar radiation

Design of graphene membrane

2D Graphene

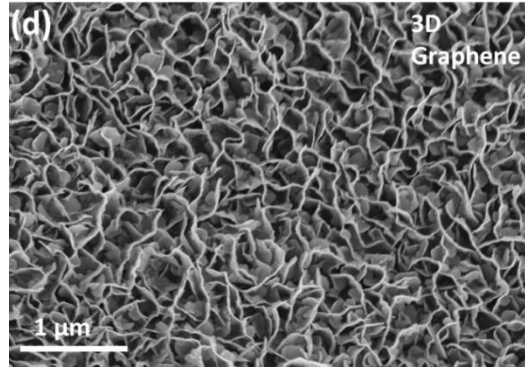
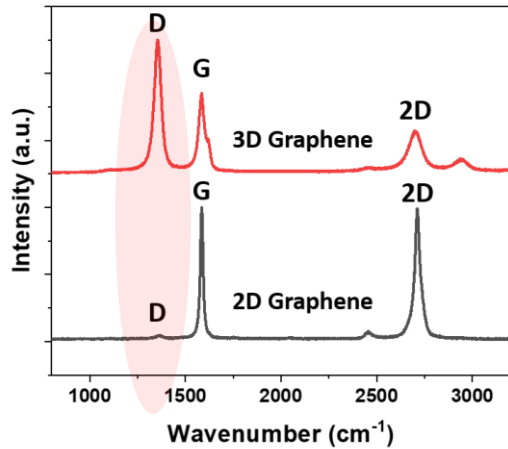


3D Graphene



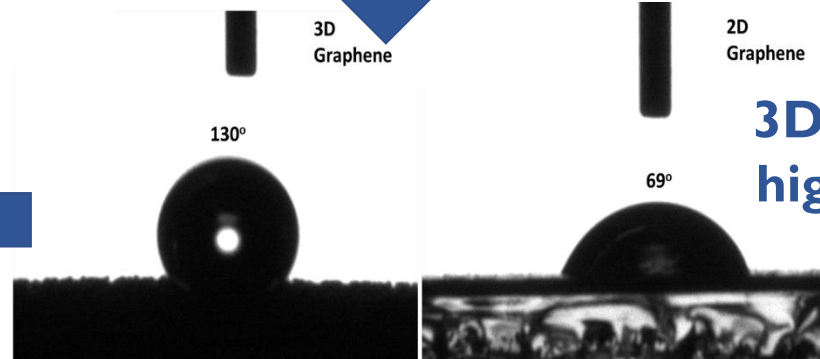
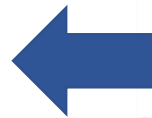
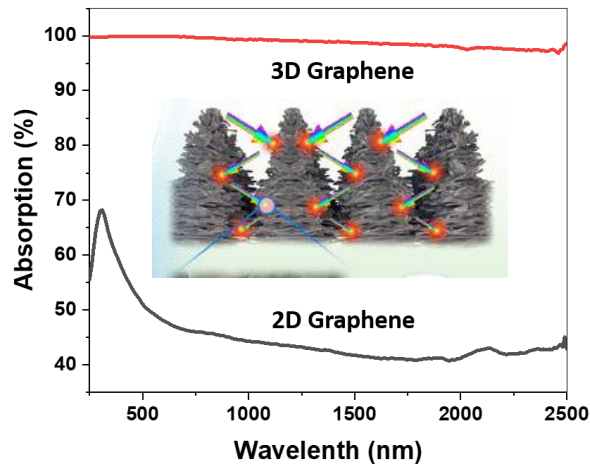
Characterization of Graphene Membranes

D peak in the 3D-G film is a result of the open edges found in the vertically orientated flakes



3D-G present a orientated material of the forest-like network.

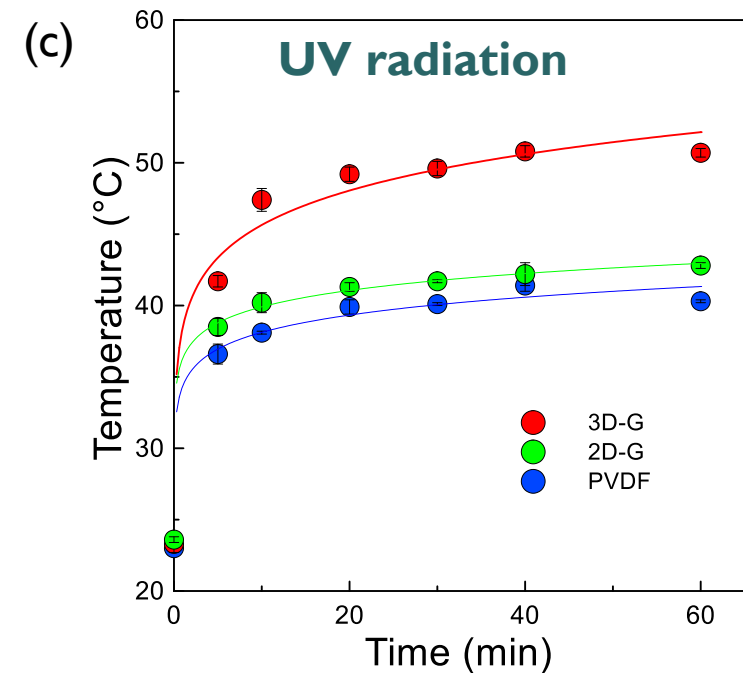
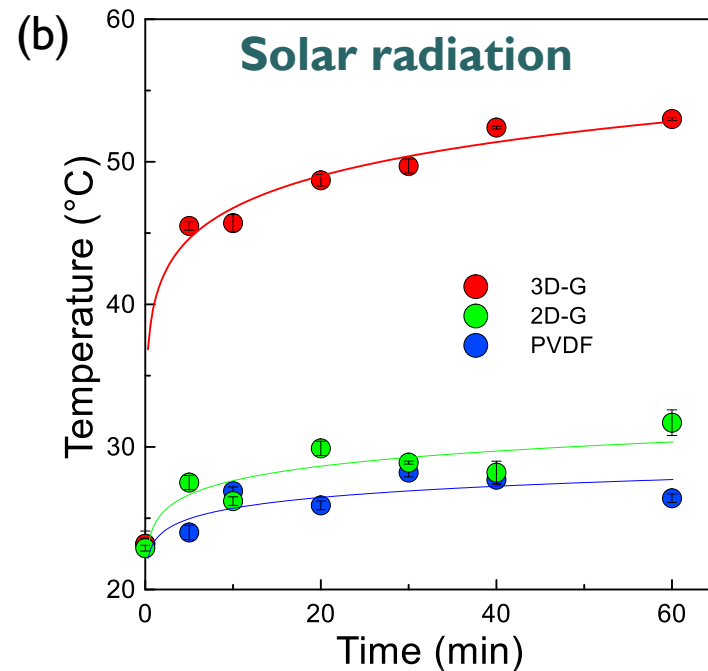
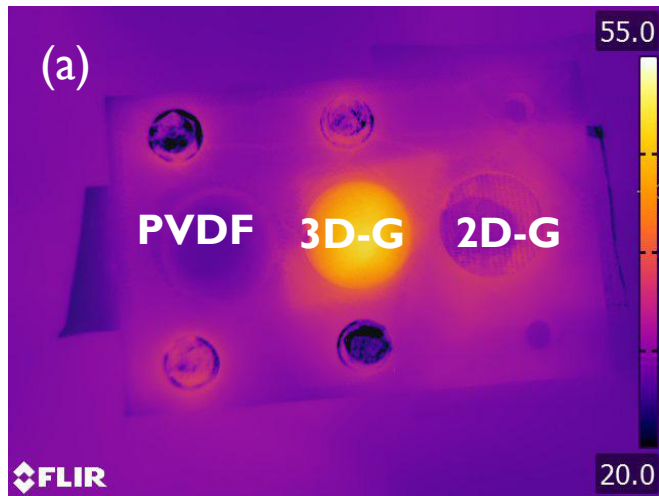
3D-G membrane absorbs 99,8% of UV-Vis-NIR



3D-G membrane is highly hydrophobic

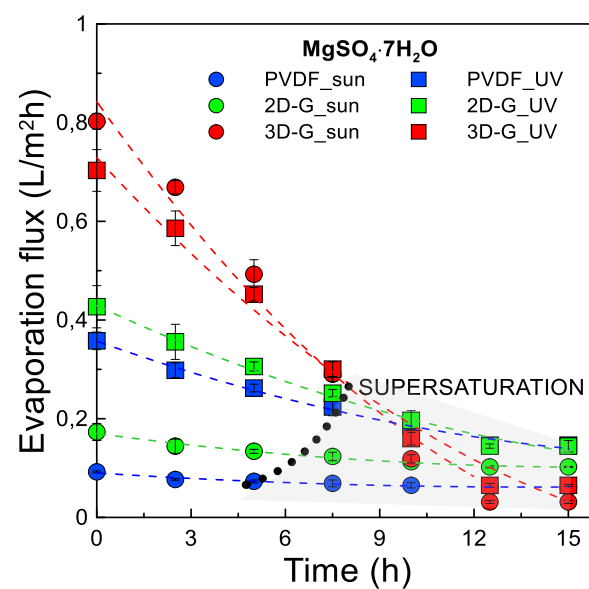
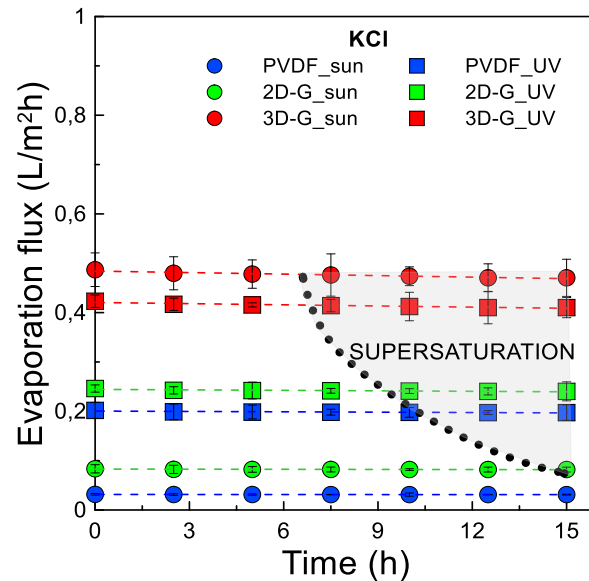
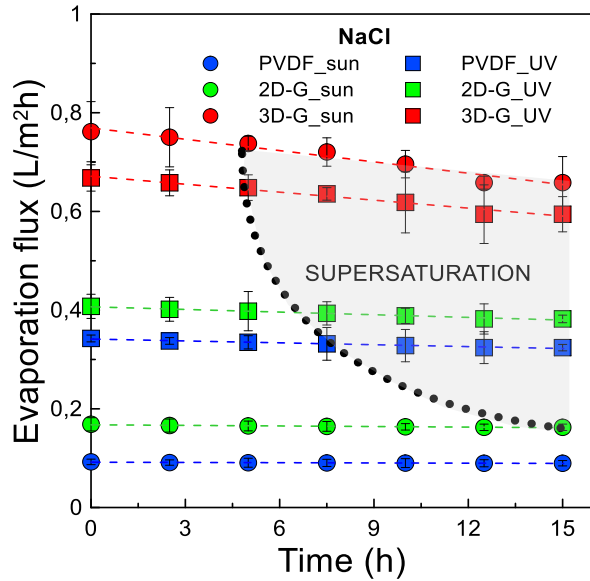
Photothermal effect

3D-G membranes reached 53°C under the equivalent of 1 sun solar radiation in less than an hour; 24°C higher than the surface temperature measured for the other surfaces.

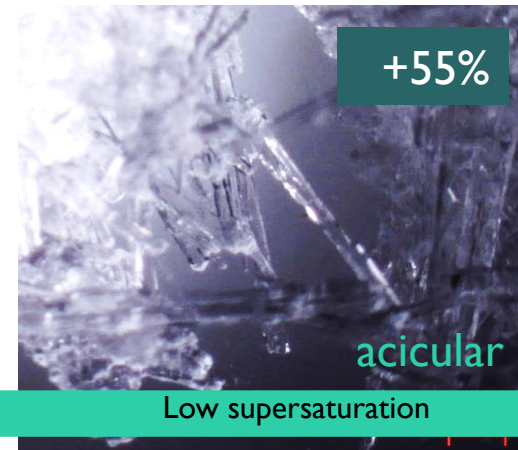
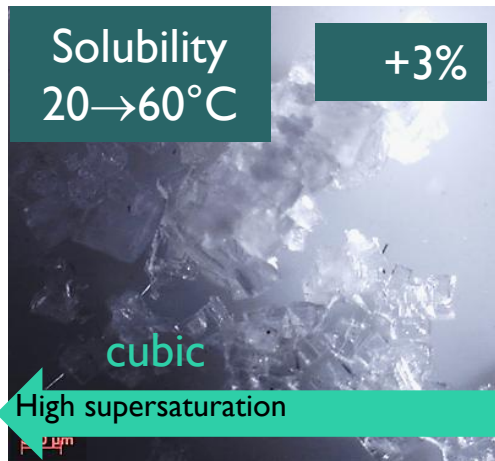


(a) Infrared pictures of PVDF, 2D-G and 3D-G membranes under solar radiation; Evolution in time of the temperature profile of PVDF, 2D-G and 3D-G under solar radiation (b) and UV-light (c)

The advent of photothermal membrane crystallization



Photothermal membrane enabled the dehydration of the brine inducing supersaturation conditions responsible for salt crystallization

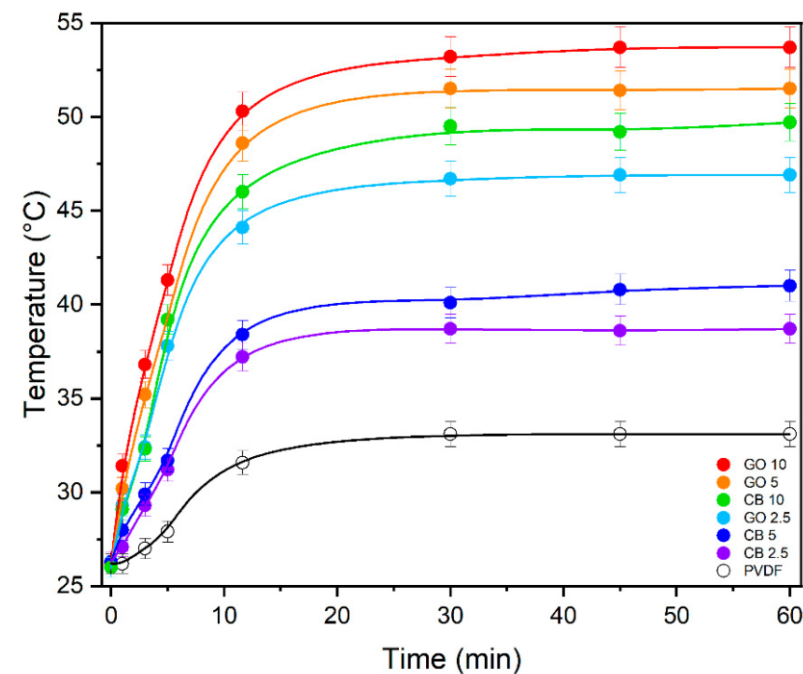
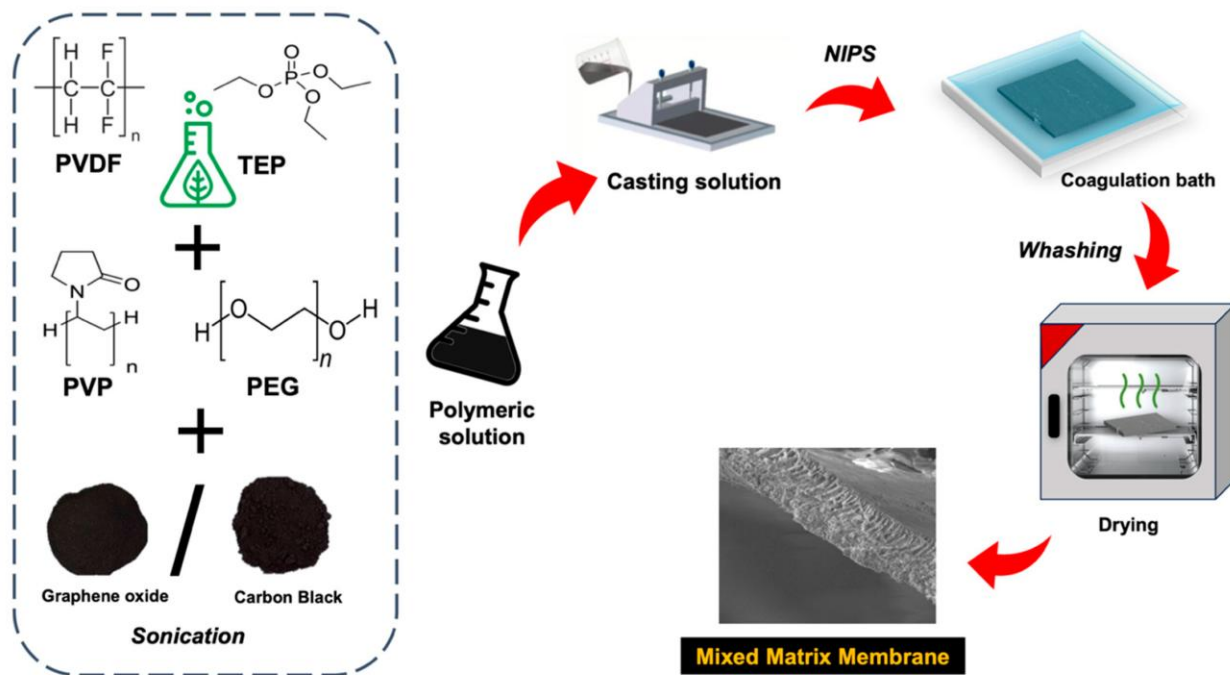


Poor Scalability (plasma treatment)

Santoro et al., *J. of Colloid and Interface Science*, 2022, 623, 607-616

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Graphene-based mixed matrix membranes

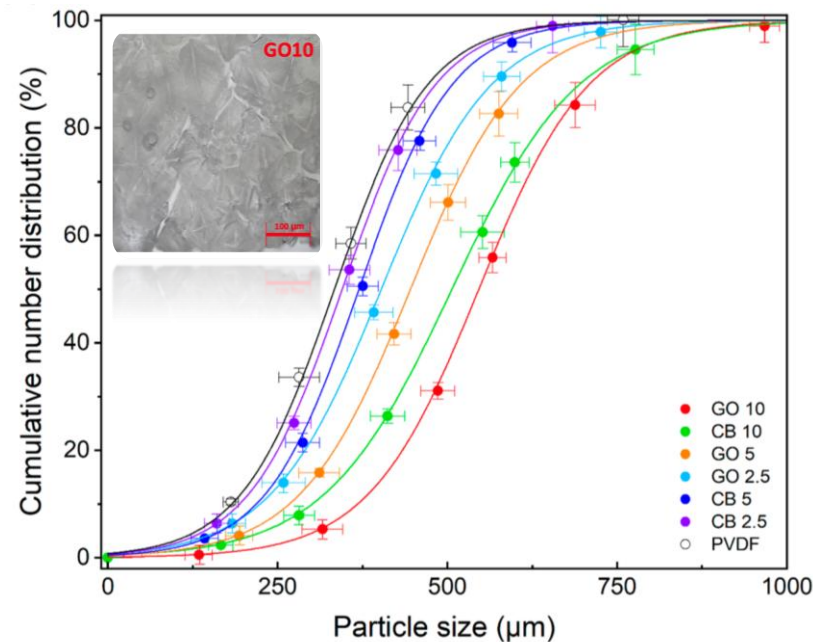
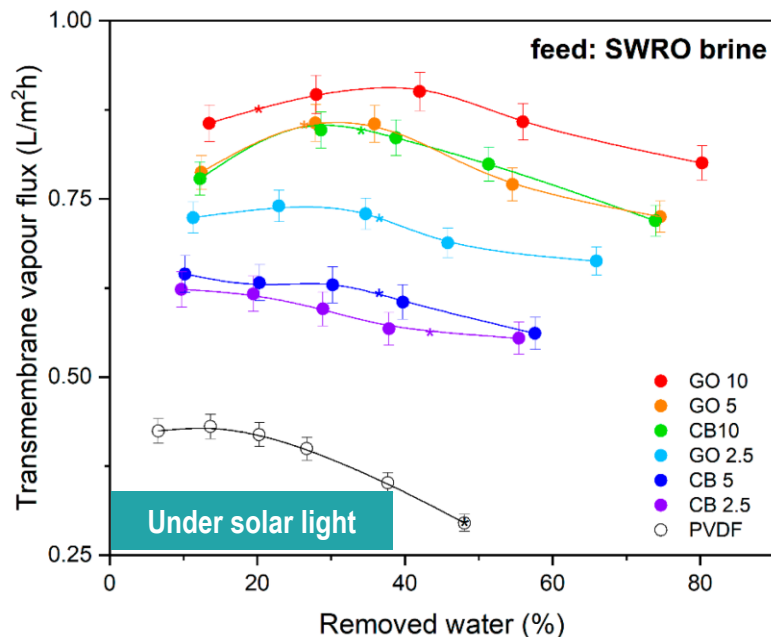


The dispersion of graphene oxide (GO) or Carbon black (CB) enabled the development of photothermal membranes hitting a temperature of ca, 55°C under the solar radiation (10wt,% of GO).

Halite extraction from SWRO brine

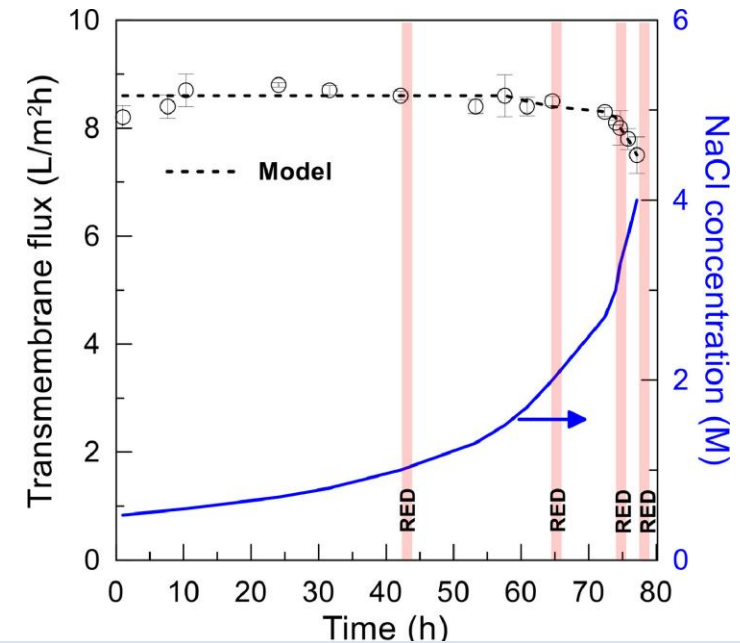
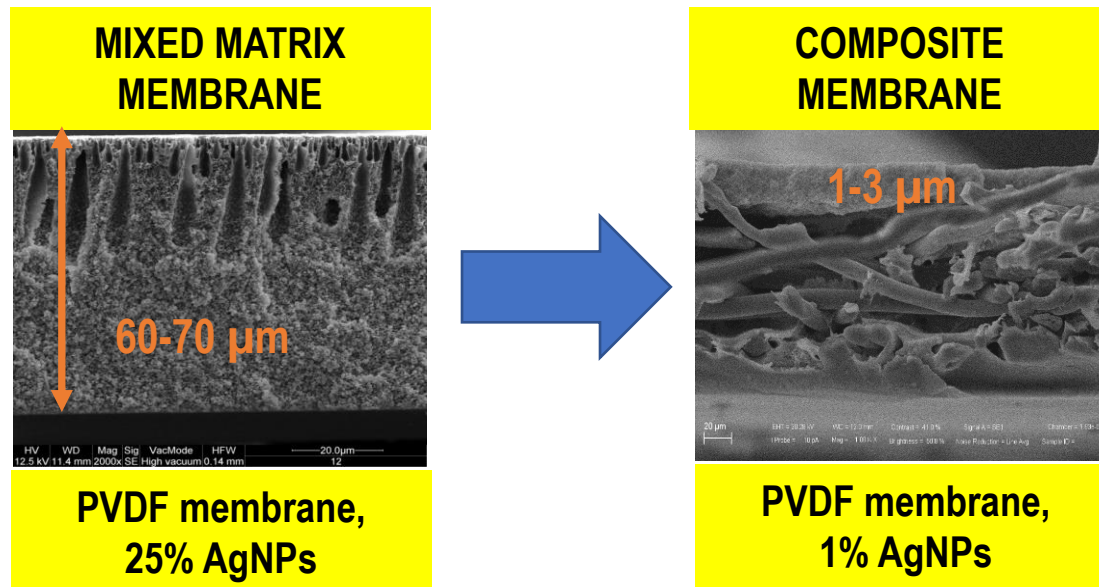
Light-to-heat conversion was used in PhMCR experiments to facilitate the evaporation of water from the SWRO brine to supersaturation, leading to sodium chloride (NaCl) nucleation and crystallization.

SWRO brine was pre-treated with sodium bicarbonate (NaHCO_3) to achieve a $\text{CO}_3^{2-}/\text{Ca}$ molar ratio of 1.3. This procedure is essential to reduce the risk of inorganic scaling, which is primarily caused by calcium-based compounds.



- GO10 photothermal membrane:**
- ❖ Crystal size of ca. 500 μm
 - ❖ Coefficient variation of ca. 60%
 - ❖ Yield of crystallization of ca. 25%

From mixed matrix membranes to composite membranes

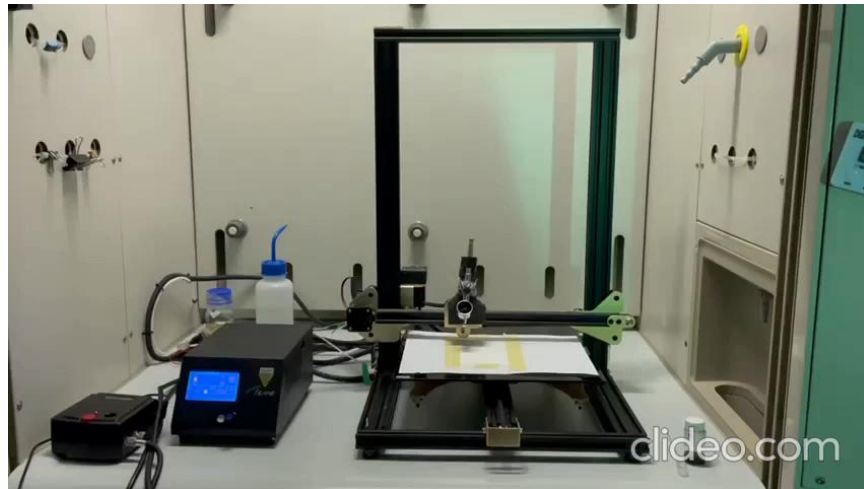
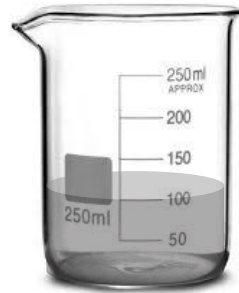


- ✓ PhMD allowed to hit a recovery factor of 87.5% obtaining a hypersaline brine (4 M) as retentate (blue energy generation?)
- ✓ Membrane Cost: 3-4 \$ m⁻²
- Specific thermal energy consumption above 700 KW m⁻³ (Irradiance of UV lamp= 6400 W m⁻²)

Composite Graphene-based membranes

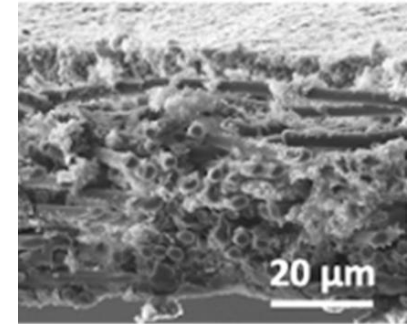
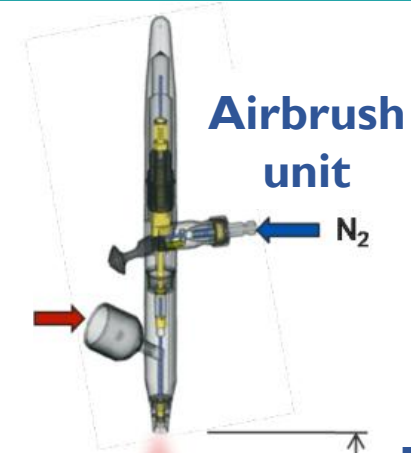
Polymeric Solution

**5wt%
Polydimethylsiloxane
(PDMS)
+
0,05-0,5 wt% of GO**



Spray Coating

**10 mL of
Polymeric
Solution**

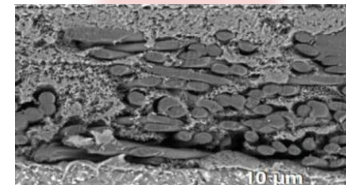


**~5 min
(X 3)**

10 cm

**Planar motion at a
velocity 60 mm s⁻¹**

**PVDF
membrane
~100 cm²**

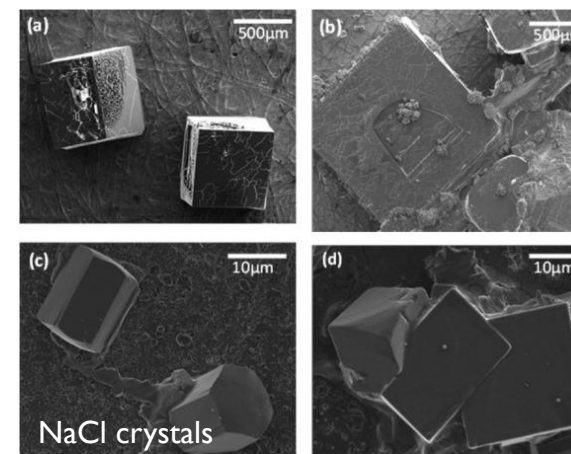
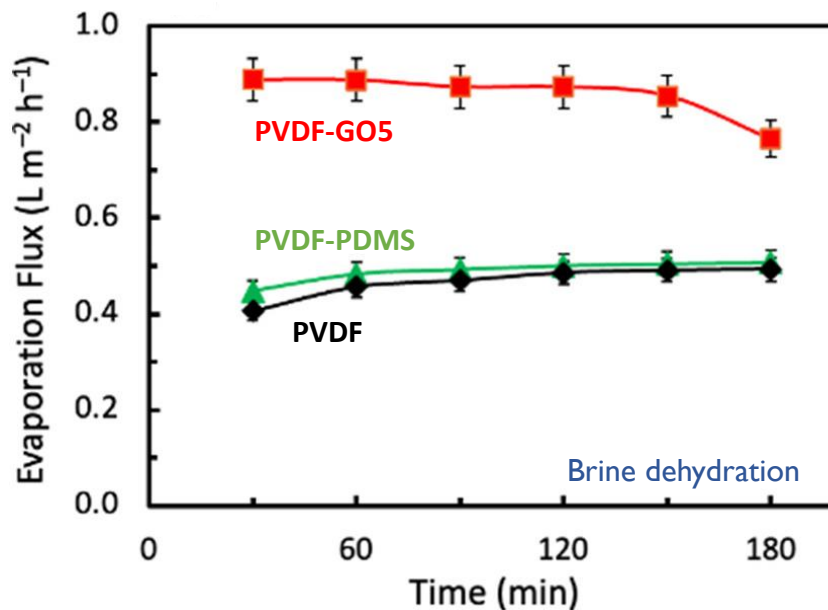
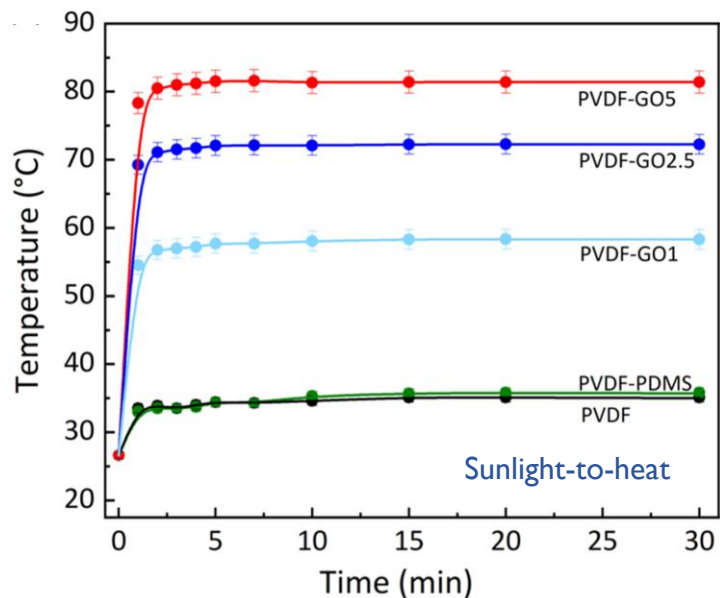


Embaye et al., Desalination 608, 2025, 118847

Graphene-based composite membranes

Membrane type	Largest pore size (μm)	Smallest pore size (μm)	Mean Pore size (μm)	Porosity (%)	Thickness (μm)	Ra (nm)	RMS (nm)
PVDF	0.92 ± 0.01	0.36 ± 0.06	0.45 ± 0.06	69.54 ± 2.3	163 ± 3	413 ± 149	515 ± 172
PVDF-PDMS	0.83 ± 0.02	0.29 ± 0.01	0.40 ± 0.03	69.31 ± 1.8	180 ± 4	315 ± 74	395 ± 79
PVDF-GO5	0.90 ± 0.01	0.29 ± 0.03	0.39 ± 0.01	67.90 ± 0.6	182 ± 4	469 ± 97	584 ± 124

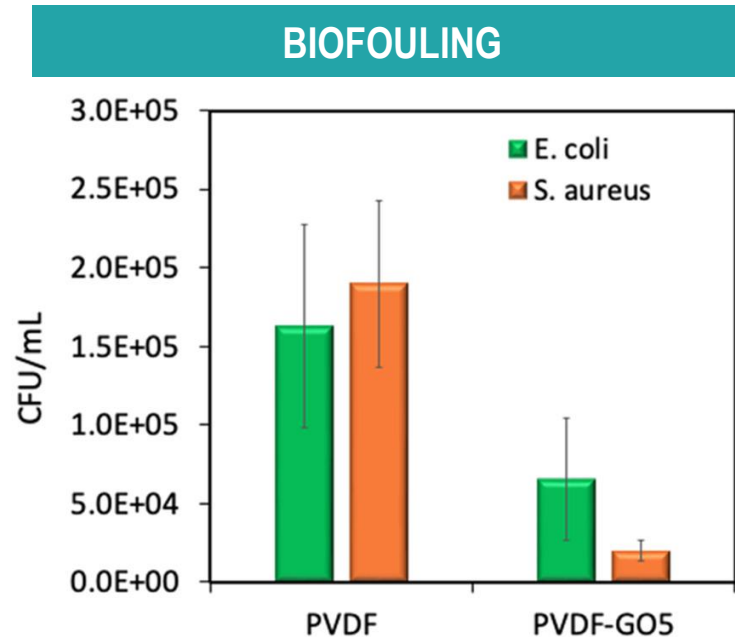
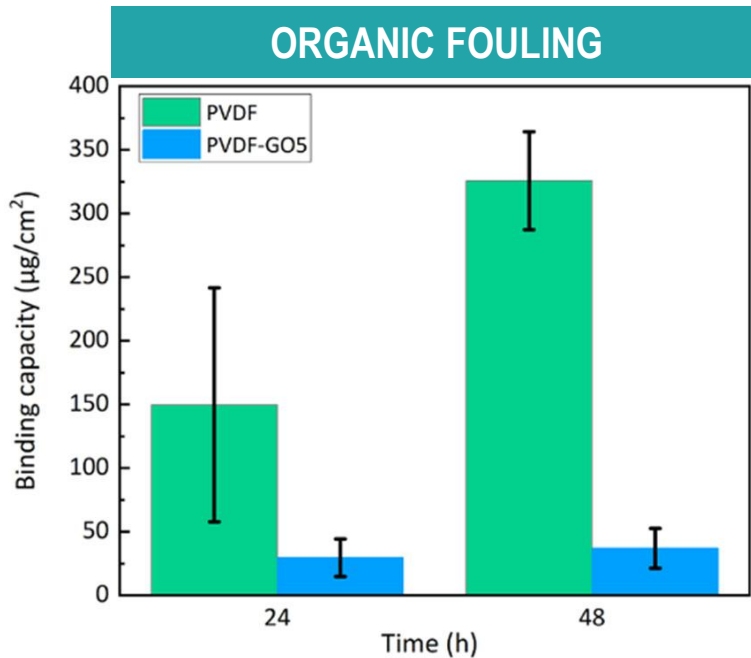
average roughness (*Ra*) and root mean square (*RMS*)



Embaye et al., Desalination 608, 2025, 118847

Antifouling behavior

Membrane type	Contact angles (°)			Surface energy values (mJ/m ²)				
	Water	Glycerol	Diiodomethane	γ^{LW}	γ^+	γ^-	γ^{AB}	γ^{Tot}
PVDF	133	115	99	8.90	0.14	0.79	0.66	9.57
PVDF-GO5	137	146	135	1.04	0.17	1.90	1.14	2.18



membrane-foulant interactions:

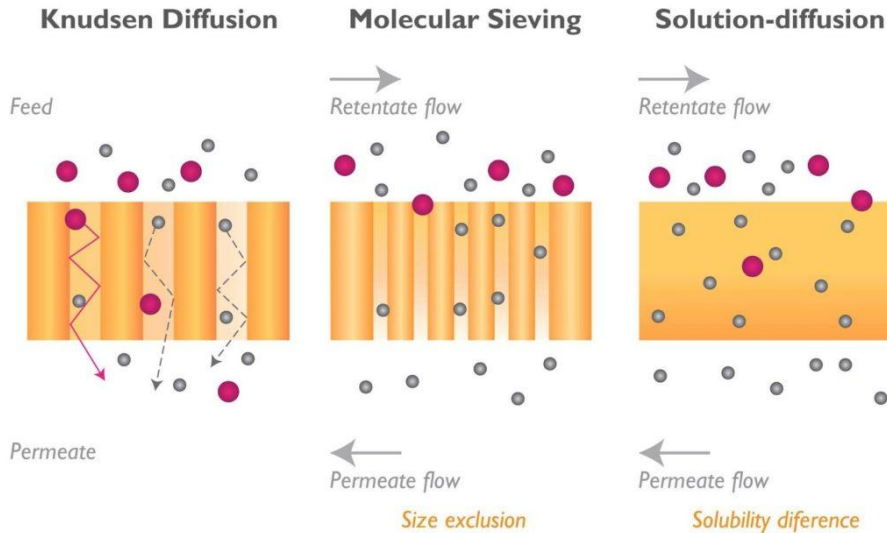
- γ^{LW} → **van der Waals** (hydrophobic interactions, non-specific fouling)
- γ^+ → **Electron acceptor** (surface acidity, interacts with bases)
- γ^- → **Electron donor** (surface basicity, interacts with acids)
- γ^{AB} → **Acid-base interactions** (mainly hydrogen bonding, polar fouling)
- γ^{Tot} → **Overall adhesion potential**

Embaye et al., Desalination 608, 2025, 118847



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Carbon Molecular Sieve Membranes (CMSMs)

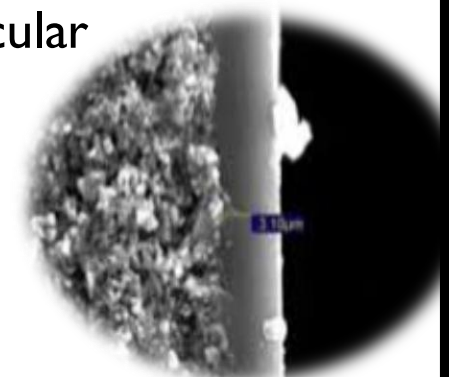


Molecular Sieving Membranes:

Sub-nanoporous membranes capable of discriminating molecules based on **size, shape, and kinetic diameter**, enabling selective molecular transport through precise nanoscale channels (size-exclusion effect).

Advantages of Carbon Molecular Sieve Membranes (CMSMs)

- **Precise Nanopore Engineering:** Tunable micropores ($\sim 0.3\text{--}0.8$ nm) for high molecular selectivity
- **Exceptional Chemical & Thermal Stability:** oxidative, acidic, and basic environments; >500 °C.
- **High Permeance and Selectivity:** pore swelling, maintaining separation efficiency.
- **Processability:** Thin-film fabrication compatible with scaling up.



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Membrane-assisted Ethylene Synthesis over Nanostructured Tandem Catalysts (MemCat)



LONG-TERM VISION

ENERGY PRODUCTION



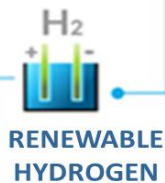
POWER PLANT



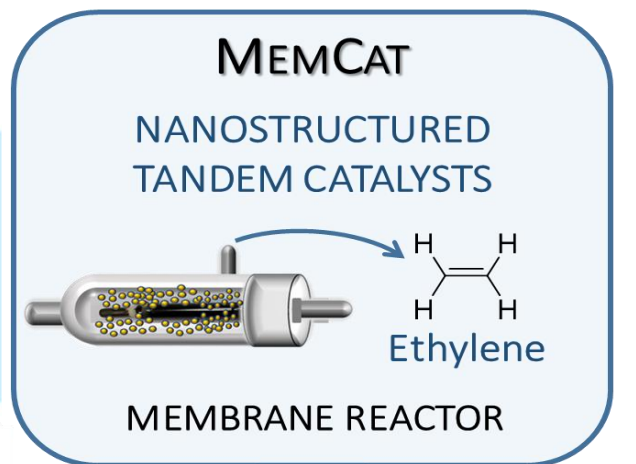
RENEWABLE
ENERGY



CCUS
ANTHROPO-
GENIC CO₂



H₂
RENEWABLE
HYDROGEN



SUSTAINABLE CONSUMER
PLASTICS

- ❖ **Objective #1:** To develop a nanostructured core@shell tandem catalyst for CO₂-to-ethylene at $\geq 80\%$ conversion
- ❖ **Objective #2:** To develop fundamental understanding of the catalytic mechanisms and the parameters affecting the conversion and selectivity of the tandem catalysts
- ❖ **Objective #3:** To develop novel temperature-resistant carbon molecular sieve membranes for ethylene production
- ❖ **Objective #4:** To demonstrate new catalytic membrane reactor prototype for selective CO₂-to-ethylene conversion
- ❖ **Objective #5:** To valorize the scientific, economic, and societal impact of the technological breakthrough innovations



Keynotes 08: Natalia Spera

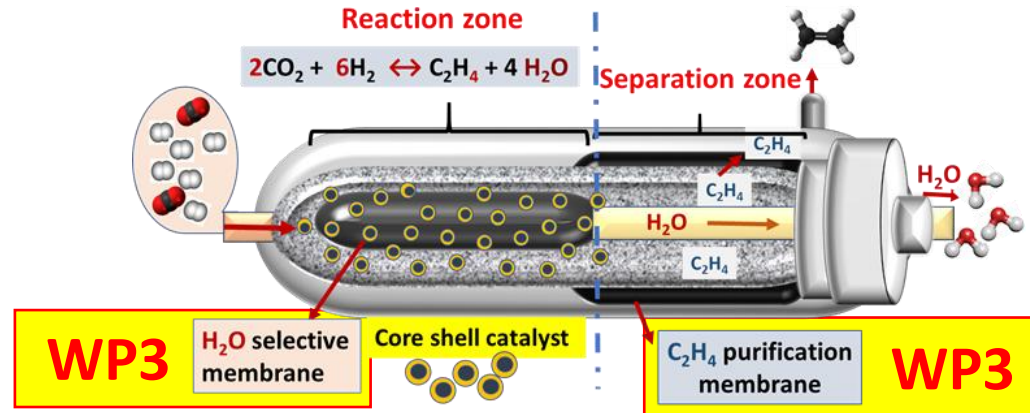
Synthesis and characterization of zeolite-CZA as a tandem catalyst for CO₂ conversion to ethylene





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Carbon Molecular Sieve Membranes (CMSMs)



❖ Objective 3: To develop novel temperature-resistant CMSMs for ET production:

- Water-gas selective CMSM to address inhibition of the competitive reverse reaction.
Target: CMSM with very high water permeance $> 1 \times 10^{-6} \text{ mol m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ and stability at $T \geq 250 \text{ }^\circ\text{C}$;
- Nanocomposite CMSM ($0.35 \text{ nm} < \text{pore size} < 0.50 \text{ nm}$) for purification permitting ET to selectively (≥ 15) pass (permeability > 5 barrier, sorption coefficient $> 0.2 \text{ cm}^3 \text{ cm}^{-3} \text{ cmHg}^{-1}$) from the product stream, the selectivity of which is increased through the incorporation of MOF, COF, and zeolite nanomaterials.

Target: Purification membrane with $\geq 15 \text{ ET/C}_3\text{H}_x$ selectivity.



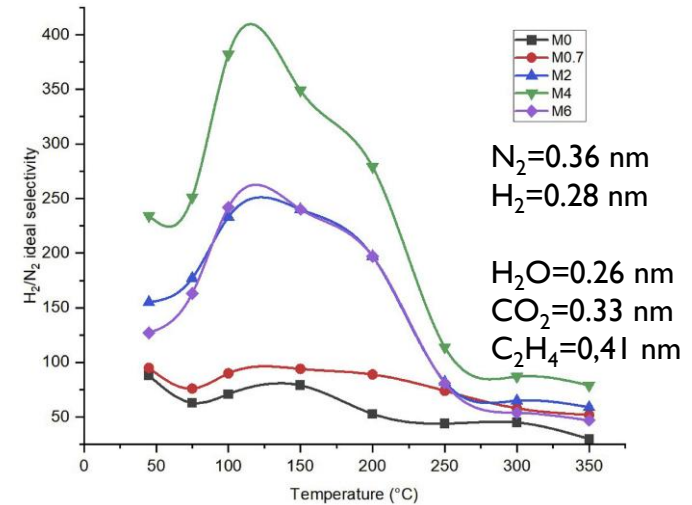
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Water-gas selective CMSM: State of Art

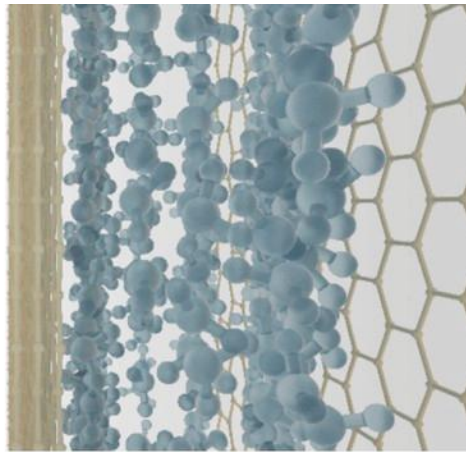
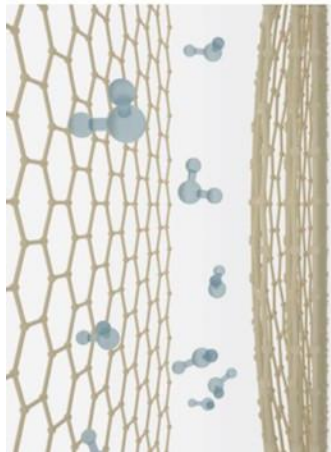


- *The developed CMSMs acted as molecular sieve for H₂/N₂ at high temperature.*
 - *It is possible to tune the pore size in order to promote the selective permeation of H₂O with respect to CO₂.*
- *Aluminum nanoparticles can improve the hydrophilicity of the CMSMs*

Molecular sieve



<https://doi.org/10.1016/j.ijhydene.2022.02.198>



Capillary condensation in hydrophilic carbon pores reduces effective pore size, enhancing selectivity by partially or fully blocking less condensable species. This mechanism can be exploited to improve water separation in gas mixtures, e.g., during CO₂ hydrogenation.

<https://physicsworld.com/a/capillary-condensation-follows-classical-law-even-at-the-nanoscale/>

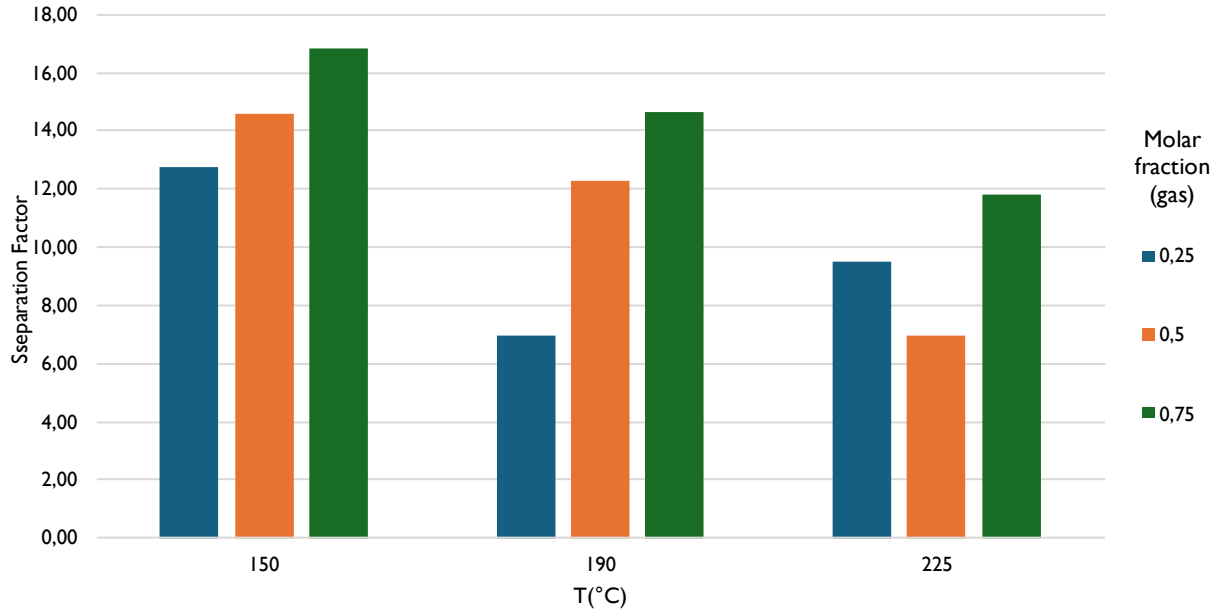


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Preliminary results



H₂O/CO₂



T (°C)	H ₂ O permeance (mol · s ⁻¹ · Pa ⁻¹ · m ⁻²)
150	8,8 · 10 ⁻⁰⁷
190	8,0 · 10 ⁻⁰⁷
225	9,8 · 10 ⁻⁰⁷

Molar fraction 0,75

- ❖ MemCat CMSMs showed promising results in terms of water selectivity and permeance and will be tested in catalytic membrane reactor prototype for selective CO₂-to-ethylene conversion



Presentation 12: Claudia A. Revilla Pacheco
Development of water-vapor selective CMSMs for CO₂ valorization using membrane reactors



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Conclusions



- ❖ Synergy of Carbon Nanomaterials with Membranes:

Carbon nanomaterials provide tunable properties (thermal conductivity, light absorption, selective permeability) that significantly expand the functionality of conventional membranes

- ❖ Photothermal Membranes for Brine Valorization:

Solar-driven photothermal membrane distillation enables efficient brine concentration and water recovery. A sustainable route to address both water scarcity and resource valorization

- ❖ Carbon Molecular Sieve (CMS) Membranes in Catalytic Reactors:

Precise molecular sieving and high-temperature stability make CMS membranes promising for reaction–separation integration.

- ❖ MemCat project will demonstrate early use of CMSMs to shift CO₂ hydrogenation towards ethylene production by selective removal of water

- ❖ Carbon-based membranes will be key enablers for sustainable separation and reaction technologies.



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Membrane-assisted Ethylene Synthesis over Nanostructured Tandem Catalysts



Thank you for your attention

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