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Advanced Membrane Technology Research Centre

DISSEMINATION WORKSHOP ON MEMBRANE TECHNOLOGY, 21 JULY 2018, DORSETT HOTEL KL

THIN FILM NANOCOMPOSITE MEMBRANES

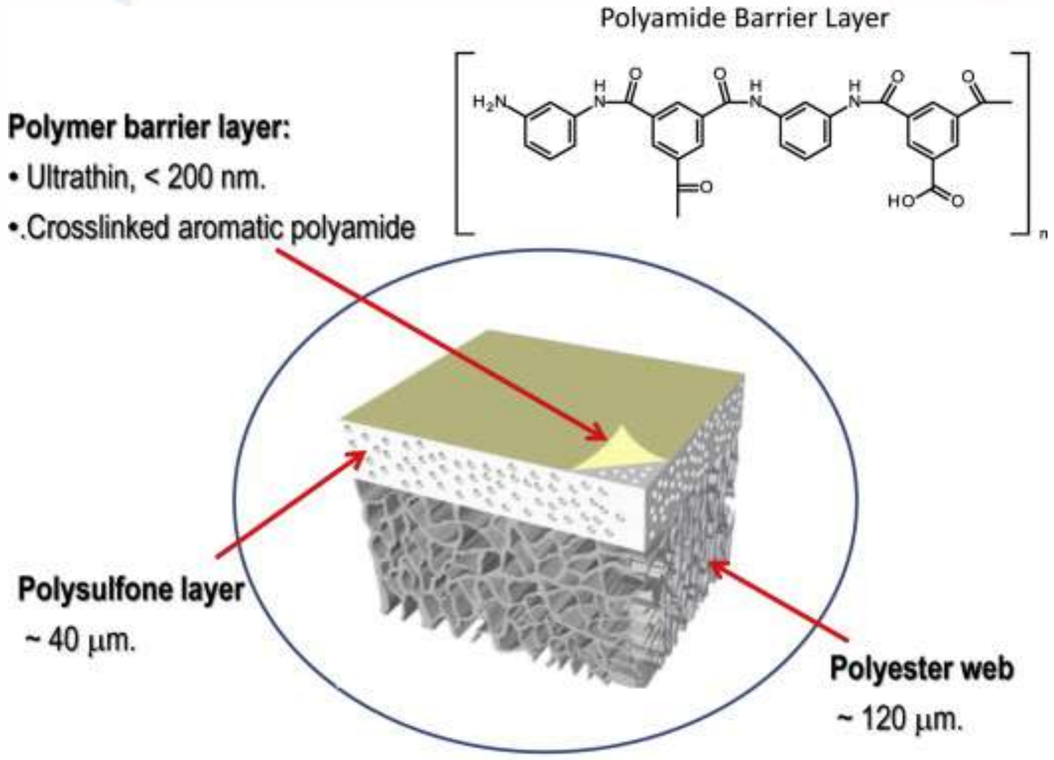
GOH PEI SEAN
Advanced Membrane Technology Research Centre (AMTEC),
School of Chemical and Energy Engineering, Faculty of Engineering
Universiti Teknologi Malaysia

PRESENTATION OVERVIEW

1. Development of TFN
2. Nanomaterials in TFN
3. Current Advances in TFN Research
4. Challenges and Strategies for Commercialization

DEVELOPMENT OF TFN MEMBRANES

THIN FILM COMPOSITE (TFC) MEMBRANE

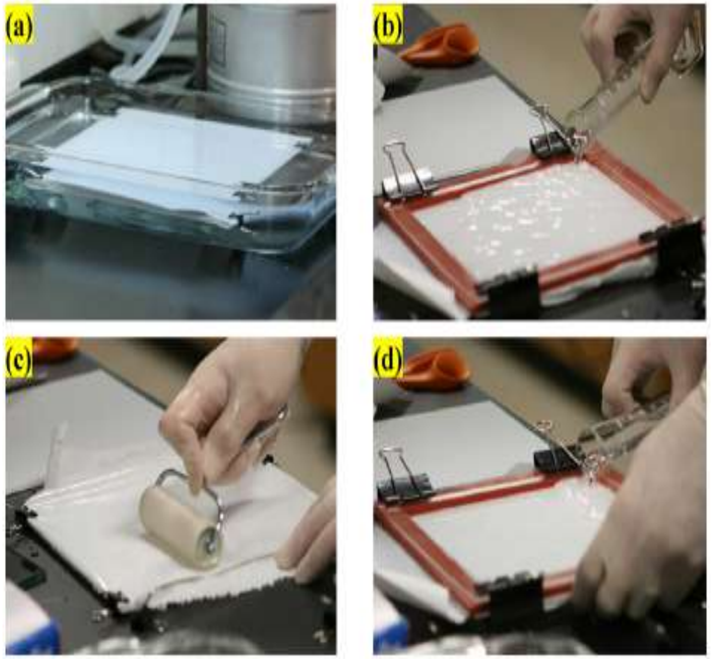


- **Polysulfone (PSf)** is the most employed material to produce an ultraporous support because it is strong, thermal and chemically stable, cheap and easily accessible

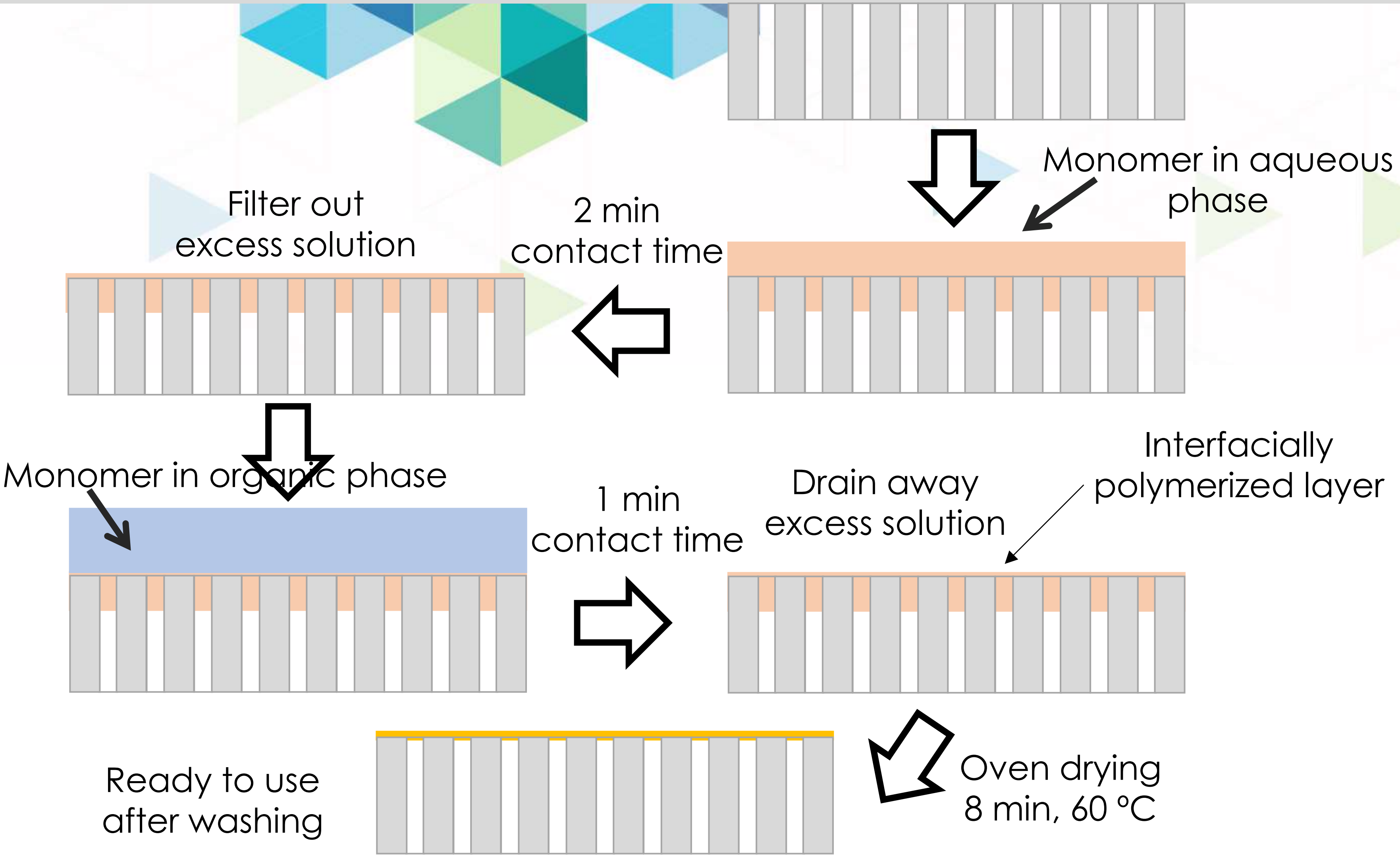
- **m-phenylenediamine (MPD) and trimesoyl chloride (TMC)** are the two most comprehensively studied monomers used to produce the PA thin film

- The performance of thin TFC fabricated via **interfacial polymerization** can be influenced by a number of parameters, such as the molecular structure and concentration of monomers, choice of organic solvent, additives used, reaction time and preparation conditions.

THIN FILM COMPOSITE MEMBRANE



Xie et al. Journal of Membrane Science. 403–404 (2012) 152–161.



THIN FILM NANOCOMPOSITE MEMBRANE

TFN membrane is a new generation of polymeric-inorganic composite membranes that are incorporated with **functional inorganic nanomaterials** with the aim of improving the characteristics of the TFC membranes

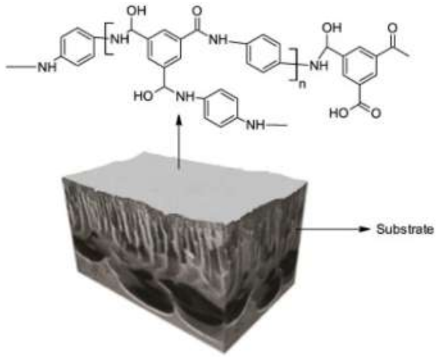
HISTORICAL DEVELOPMENT OF TFN MEMBRANE

1960-1990 → 2005 → 2010 → 2015 → 2020

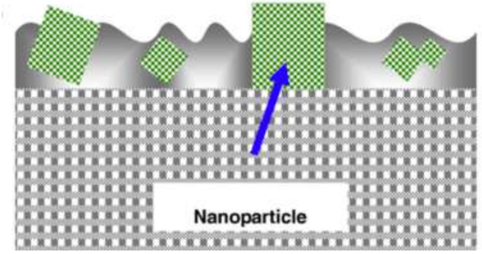
Desalination Nano-enabled Membrane Development

1963- First asymmetric cellulose acetate membrane

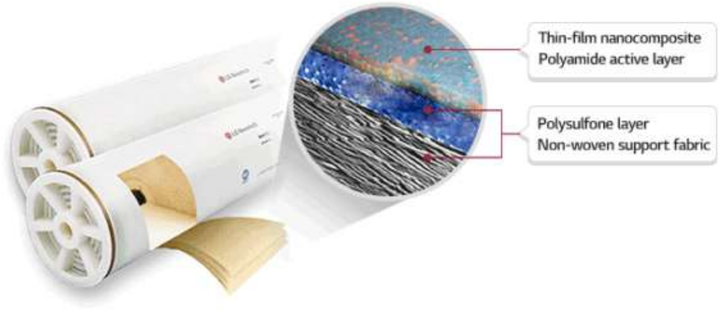
1965- First concept of interfacial polymerization for TFC



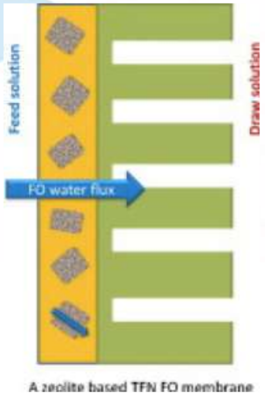
2007- First TFN (PSf/Zeolite) RO membrane



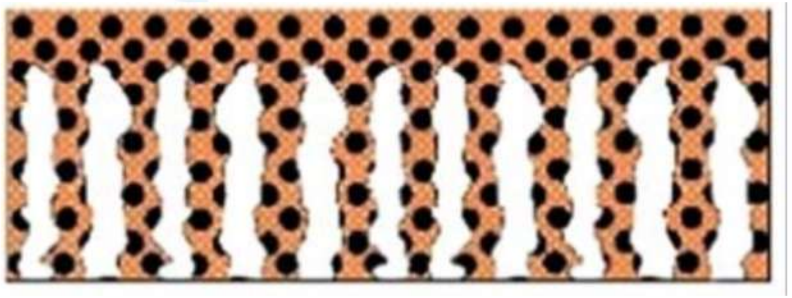
2011- Commercial TFN RO module by NanoH2O



2012- First TFN FO membrane. (PSf/zeolite)



MMM VS TFN Membranes

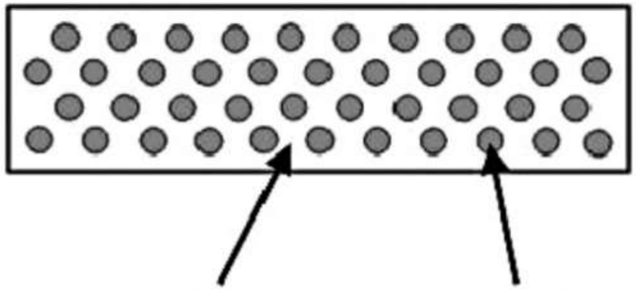


Conventional nanocomposite membrane-
Mixed Matrix Membrane

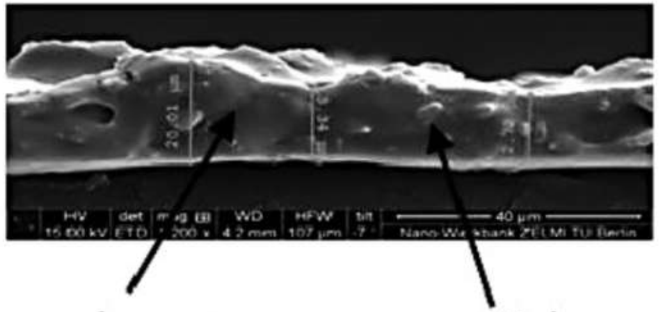
MMM belongs to a class of composite membranes consisting of a dispersed phase of inorganic fillers within a polymeric host matrix.

Prepared in 1 step phase inversion technique

Idealised MMM structure

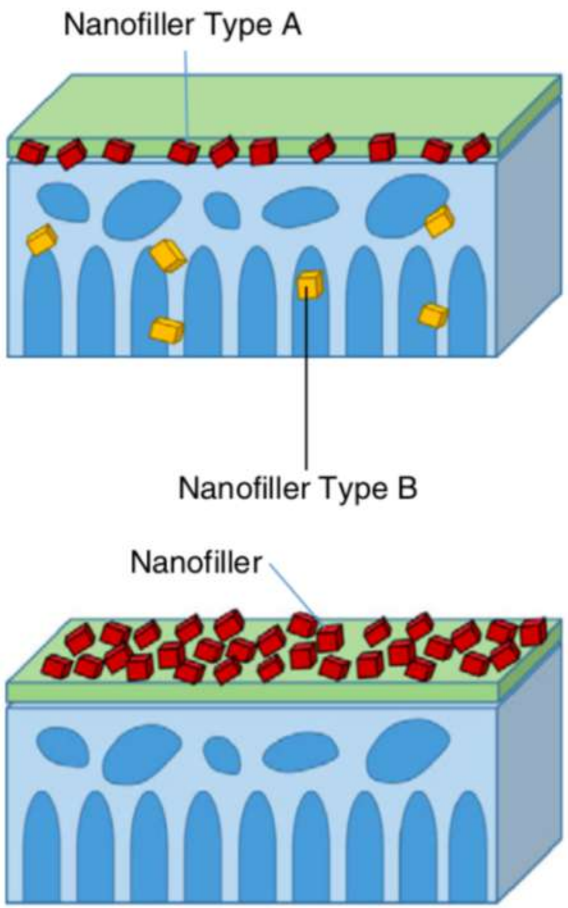


Real MMM structure:



- Randomly distributed nanofillers
- high loading is needed

THIN FILM NANOCOMPOSITE MEMBRANE

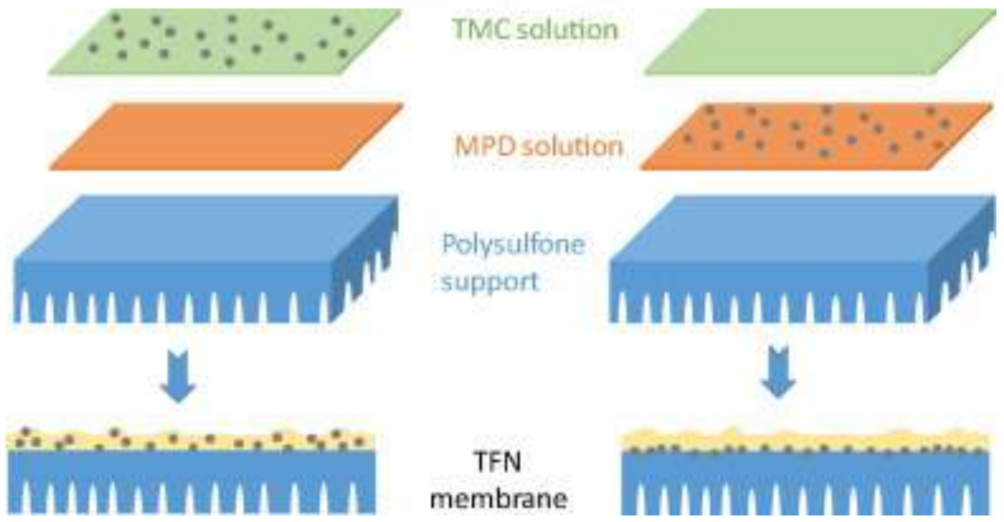


TFN provides the flexibility to modify the composite membrane layers to attain the preferred properties

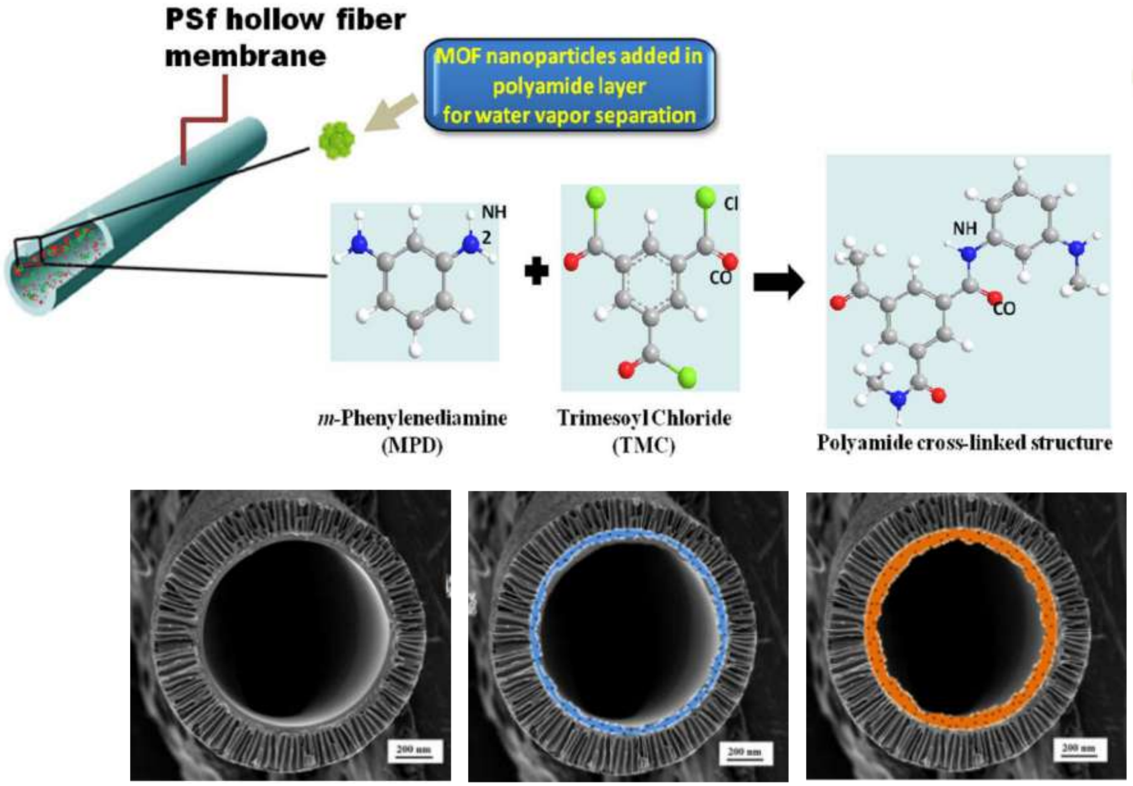
The distribution of nanofillers can be precisely controlled, i.e. deposited solely within the skin layer of the membrane during the IP process or throughout the substrate layer during the phase inversion process.

FABRICATION OF THIN FILM NANOCOMPOSITE MEMBRANE

Flat Sheets



Hollow Fibers



Ingole et al. Chemical Engineering Journal 334 (2018) 2450–2458
Plisko et al. Journal of Membrane Science. (2018) In Press

NANOMATERIALS IN TFN

WHY NANOMATERIALS

- At nano-scale, the materials show the unique size-dependent properties which are significantly different from their bulk counterparts.
- The scalable size-dependent properties of nanomaterials are related to:
  - *High specific surface area and sorption capacity*
  - *High selectivity*
  - *Fast transport*
  - *Antimicrobial*
  - *Mechanical strength*

CLASSES OF NANOMATERIALS

High hydrophilicity

- metal oxides (TiO_2, Al_2O_3, ZnO), graphene oxide
- increase productivity
- Reduce fouling of membrane

Fast Transport

- CNT, TNT, aquaporin
- Provide frictionless molecular transport to increase productivity

Antibacterial properties

- silver, copper, CNT
- Reduce biofouling of membrane

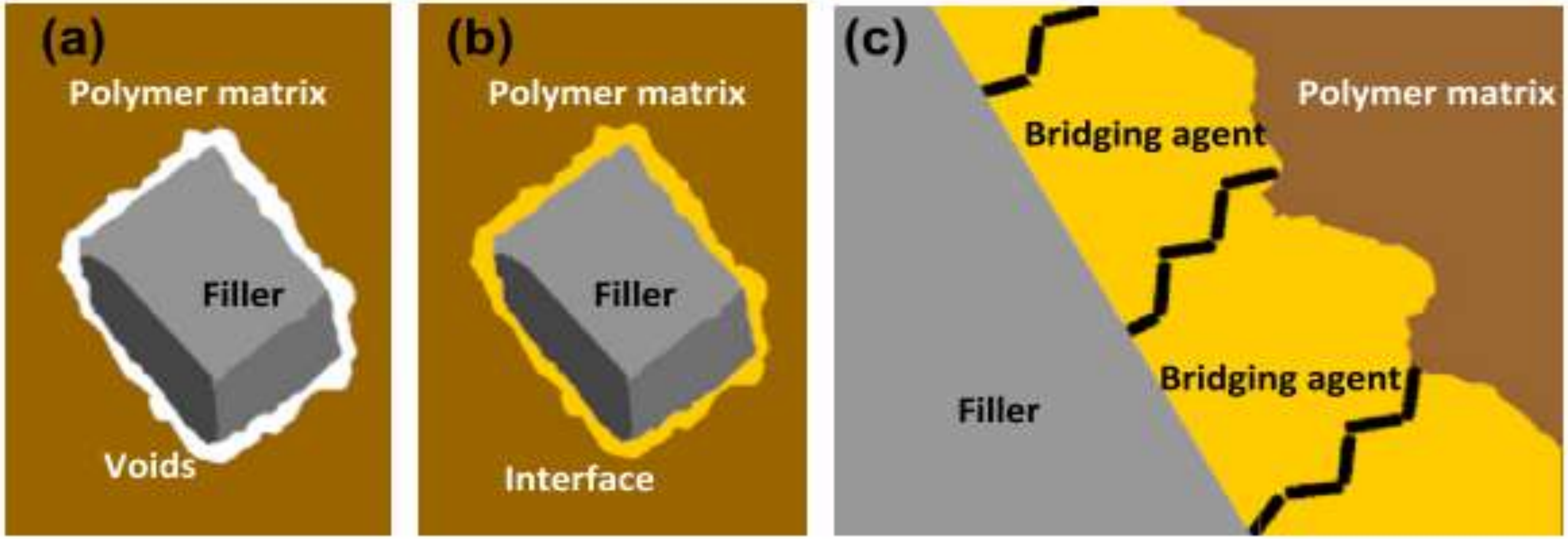
Size-exclusion

- zeolite, MOF
- 3-D structure to provide size-exclusion properties to enhance selectivity

Mechanical strength

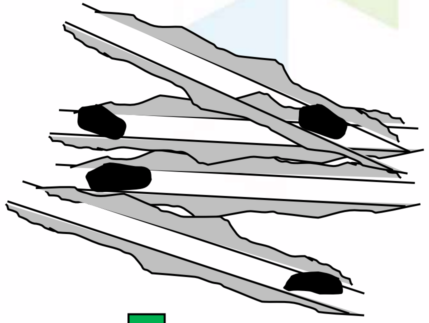
- CNT, graphene oxide
- Enhance tensile tensile strength to withstand high pressure compaction

MODIFICATIONS OF NANOMATERIALS

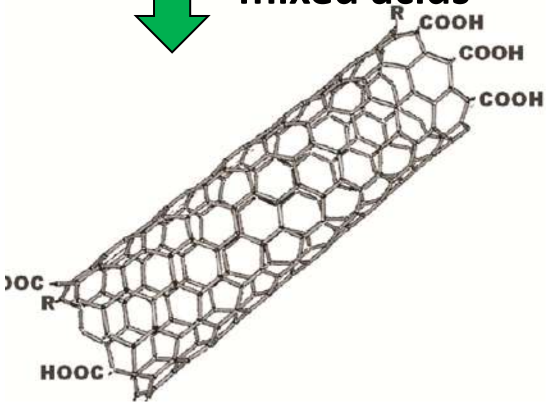


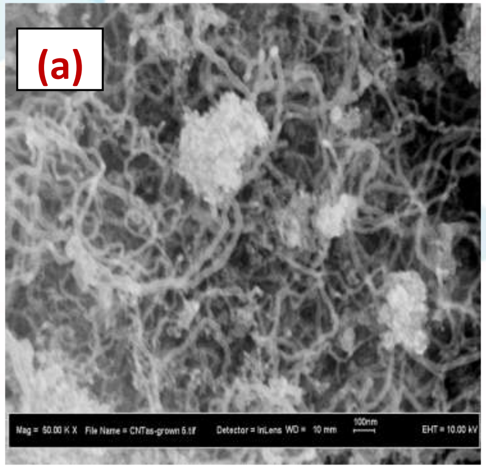
In colloidal system during fabrication, if the nanoparticles are well dispersed and more stable in organic solvent, the advantage of these nanomaterials can be maximized

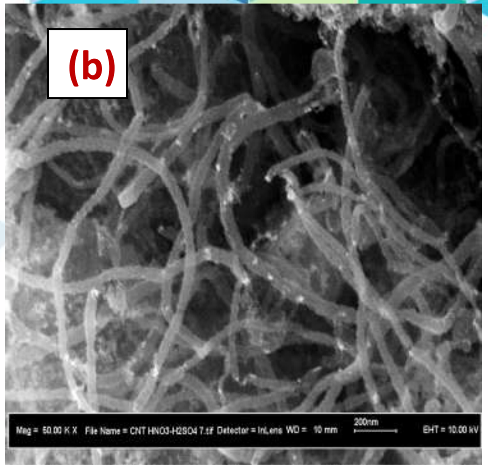
MODIFICATIONS OF CNTs



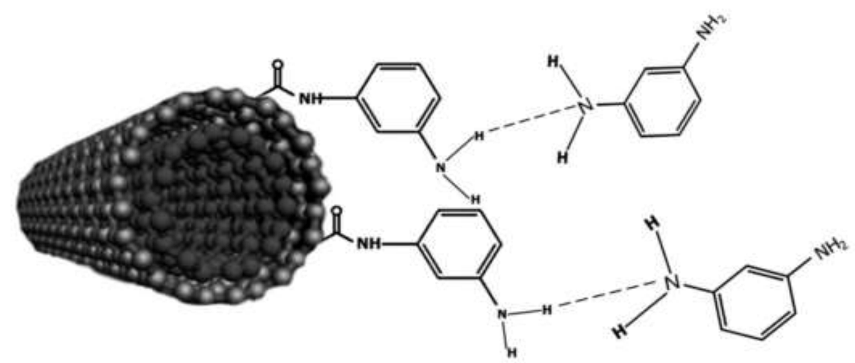
HNO_3/H_2SO_4
mixed acids





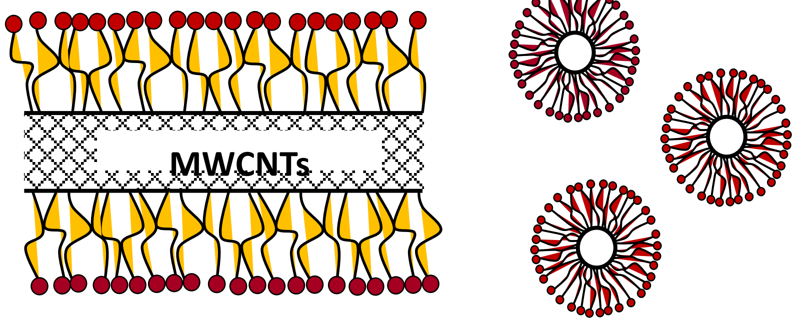


Mixed acid treatment: Chemical approach to remove impurities, reduce entanglement of CNTs and introduce functional groups to the CNT surfaces



Amine agent such as 1,3-phenylenediamine (mPDA), 1,6-diaminohexane (DAH) and 4.4′-diamino diphenyl methane (DDM) to produce the functional amine groups (NH_2) on their surfaces

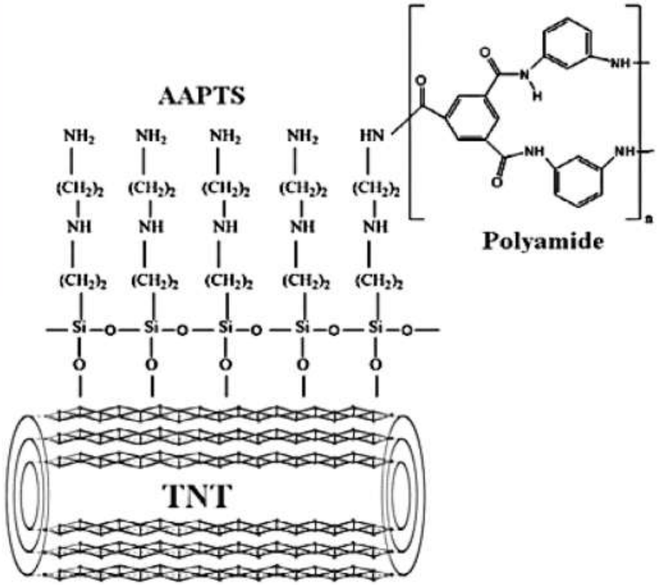
Non-ionic surfactant Triton X100



MODIFICATIONS OF METAL OXIDE NPs

Kang et al. Colloids and Surfaces A: Physicochem. Eng. Aspects 501 (2016) 24–31

Amino-functionalized TiO_2

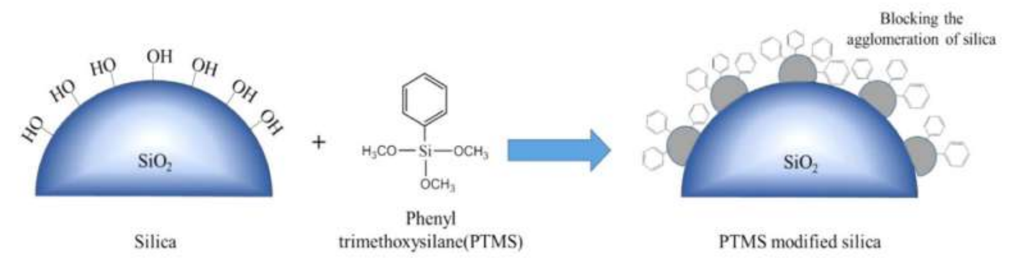


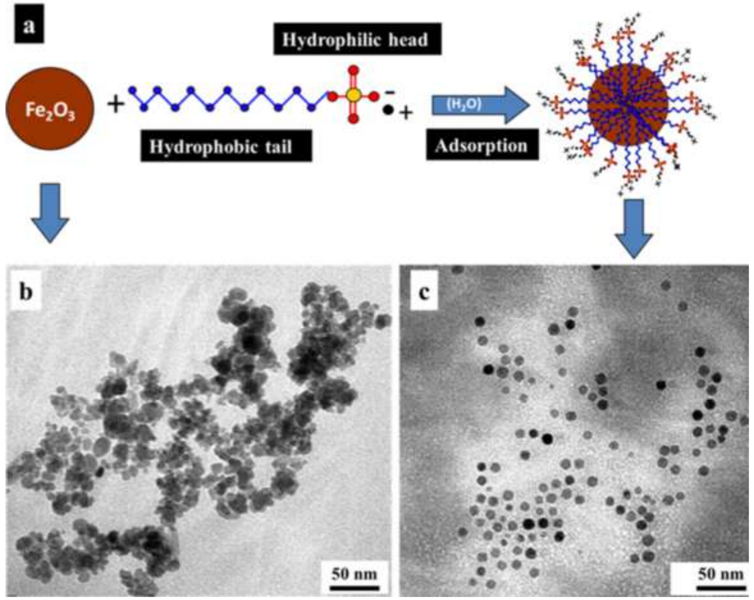
amino-functionalized TNTs might interact well with PA of TFC membrane when they are introduced during interfacial polymerization, owing to the combined action of electrostatic attraction and hydrogen bonding

Emadzadeh et al. Chemical Engineering Journal 281 (2015) 243–251

Silane-functionalized SiO_2

Modification of silica NPs with silane agent can change the hydrophilicity/ hydrophobicity of the NPs and improve their dispersion in organic solvent





Stabilization process applied to γ-Fe_2O_3 NPs using SDS surfactant.

CURRENT ADVANCES IN TFN MEMBRANE APPLICATION

LIMITATIONS IN CURRENT MEMBRANE TECHNOLOGY

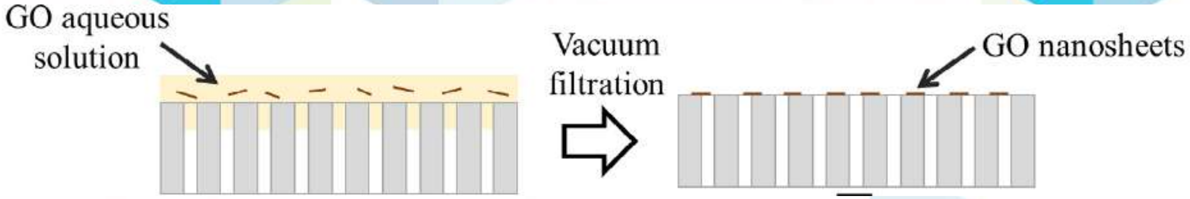
LIMITATIONS IN MEMBRANE-BASED LIQUID SEPARATION

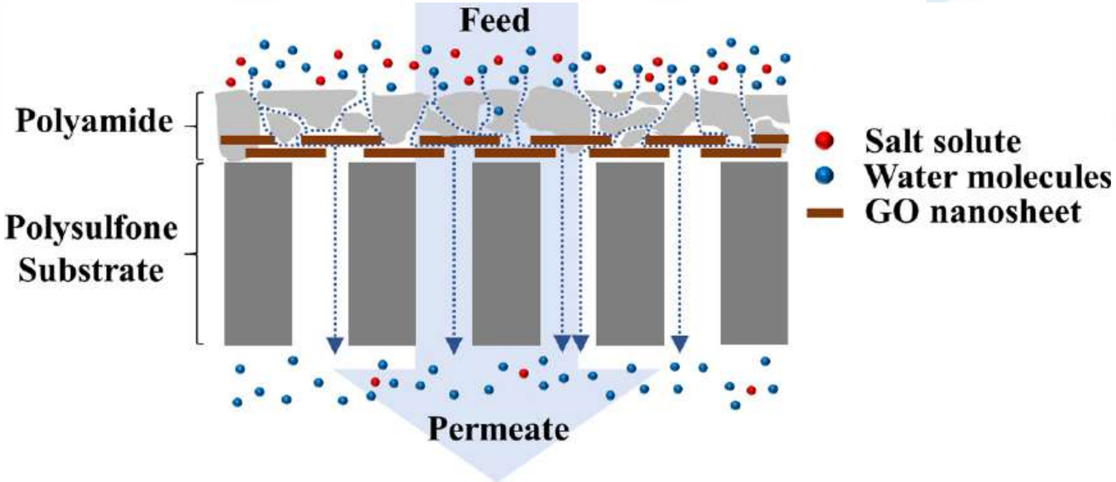
- Susceptible to fouling
- Rejection-flux trade off
- Low resistant to pressure compaction
- Frequent washing-Short membrane life-high energy consumption

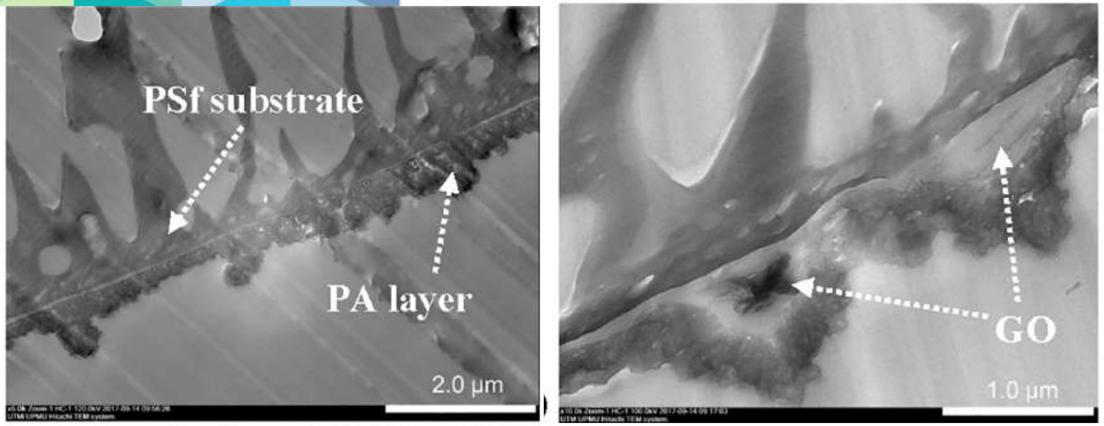
LIMITATIONS IN MEMBRANE-BASED GAS SEPARATION

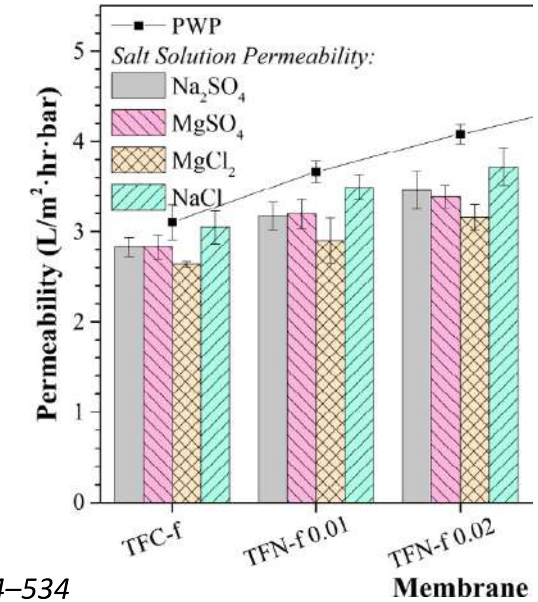
- Robeson Tradeoff
- Plasticization & swelling
- Thermal and Mechanical stability to withstand harsh operation

PSF/GO TFN for Water Softening









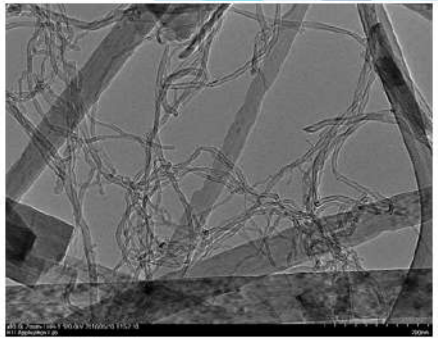
The flux of GO-TFN (0.02 wt% GO) is increased by 30% compared to TFC counterpart, up to 4.45L/m2·h·bar without compromising the salt rejection. (95.8% and 97.7% rejection against Na_2SO_4 and $MgSO_4$, respectively.)

Role of GO:
Increase hydrophilicity to improve flux and mitigate fouling

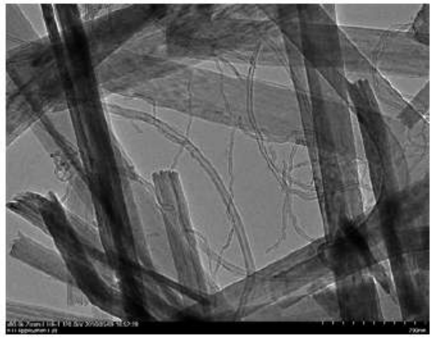
GO is introduced on top of PSf substrate through vacuum filtration method, followed by interfacial polymerization to form polyamide layer.

G.S. Lai, W.J. Lau, P.S. Goh, AF. Ismail Chemical Engineering Journal 344 (2018) 524–534

PSF/MWCNT-TNT TFN for Desalination



MWCNT-TNT

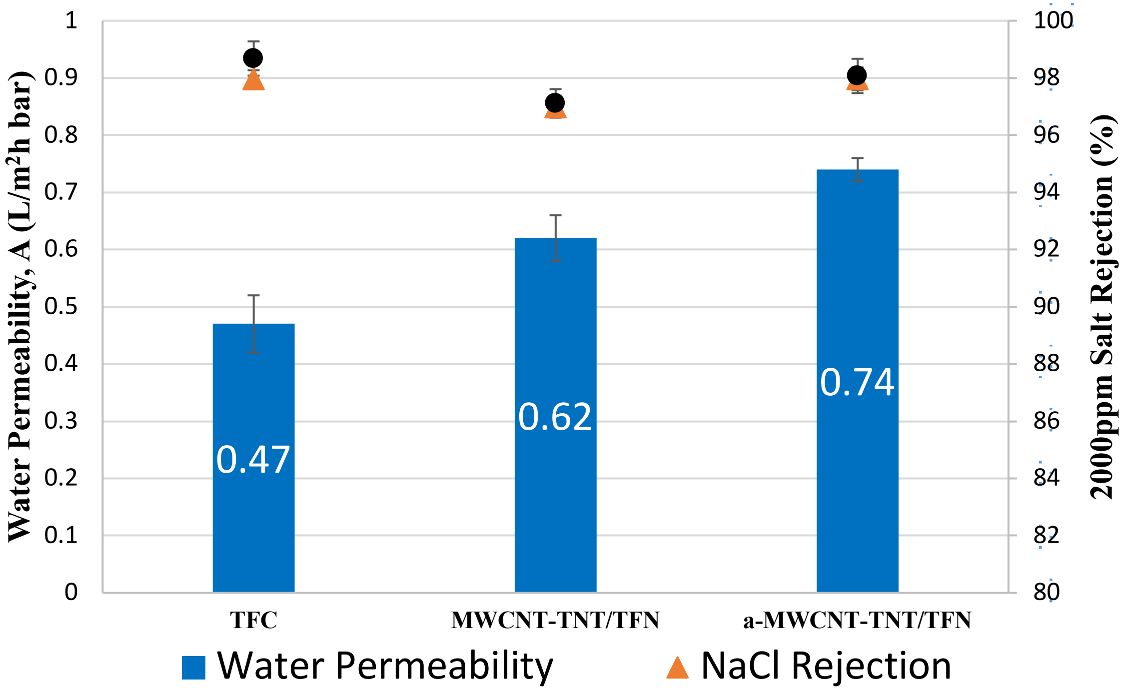


a-MWCNT-TNT

MWCNT-TNT hybrid was synthesized by hydrothermal method (ratio MWCNT:TiO2=1:5) followed by acid treatment using HCl

Type of nanoparticle	Charge
MWCNT-TNT hybrid	-8.95 mV
a-MWCNT-TNT hybrid	26.60 mV

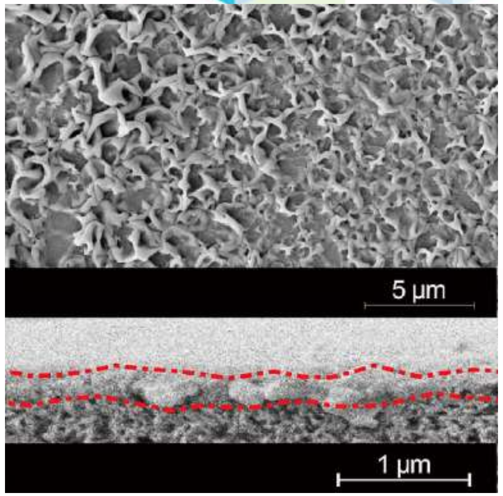
a-MWCNT-TNT improved the surface properties of the membrane in term of surface charge, surface roughness and contact angle.



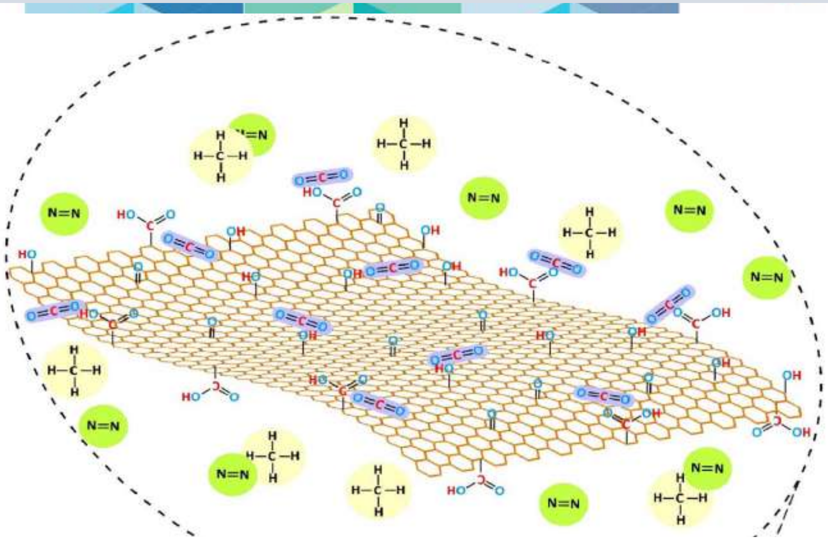
The highest water permeability of 0.74 L/m2 h bar was achieved for the TFN membrane containing 0.05 wt% acid treated MWCNT-TNT, which is approximately 57.45% than that of the neat TFC membrane.
The NaCl and Na2SO4 rejection of this membrane was 97.97% and 98.07%

I.Wan Azelee, P.S. Goh et al. Journal of Cleaner Production 514 (2018) 622-635

Highly Permeable and Selective PSF/GO for Carbon Dioxide Removal



Surface and cross sectional morphology of TFN with GO introduced to the PA layer through interfacial polymerization. Substrate consist of PSF porous membrane



Role of GO:

•Gas molecules can take advantage of the smooth graphitic surface of GO to slip across the film layer rapidly -CO2 could access the passages more easily.

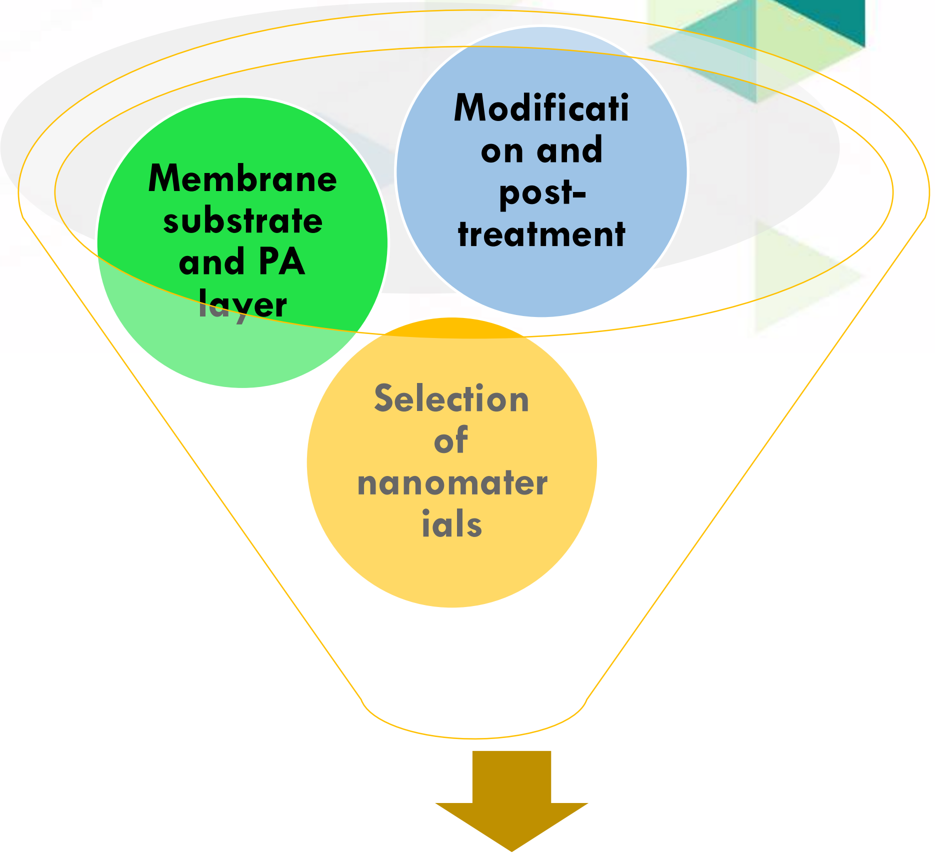
•Functional groups on GO led to higher CO2 solubility in the membrane which in turn increase the gas permeance.

•The best sample, TFN with 0.5 GO, exhibited CO2 permeance of 92.4 GPU with CO2/N2 and CO2/CH4 separation factor of 41 and 25 respectively.

KC Wong, PS Goh and AF Ismail International Journal of Greenhouse Gas Control 64 (2017) 257–266

CHALLENGES AND FUTURE OUTLOOK

THE KEYS FOR TFN MEMBRANE

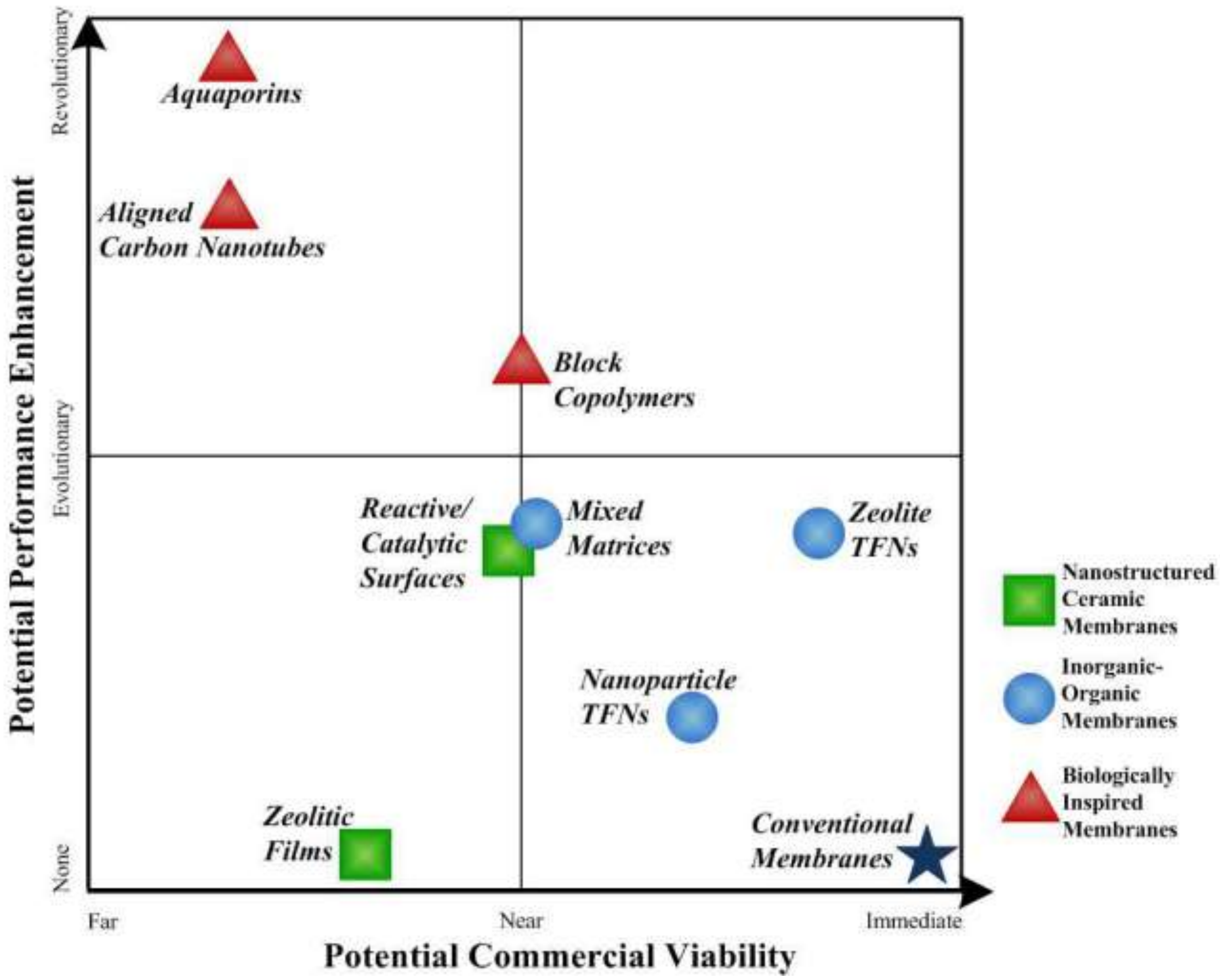


Desired TFN membrane

CHALLENGES- CLOSE THE GAPS

- Agglomeration of nanoparticles
- Alignment and orientation of nanoparticles
- Reproducibility

FUTURE OUTLOOK



CONCLUSION

- The development of TFC membrane represents a breakthrough in water and wastewater treatment (RO, FO, NF) as well as gas separation
- The introduction of inorganic fillers into TFC show attractive characteristics in improving TFN membrane in terms of productivity, selectivity, fouling and chlorine resistance.
- The main challenges encountered during TFN membrane fabrication are related to the agglomeration of nanomaterials and their poor dispersion in non-polar organic solvent
- More research in this area is still needed to develop TFN membrane with greater performance efficiency, reliability and stability for industrial implementation.

Special Thanks to

Advanced Membrane Technology Research Centre (AMTEC)
Universiti Teknologi Malaysia

Contact: peisean@petroleum.utm.my