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Engineering the re-entrant hierarchy of PDMS-PVDF membrane for membrane distillation using a facile and benign microsphere coating

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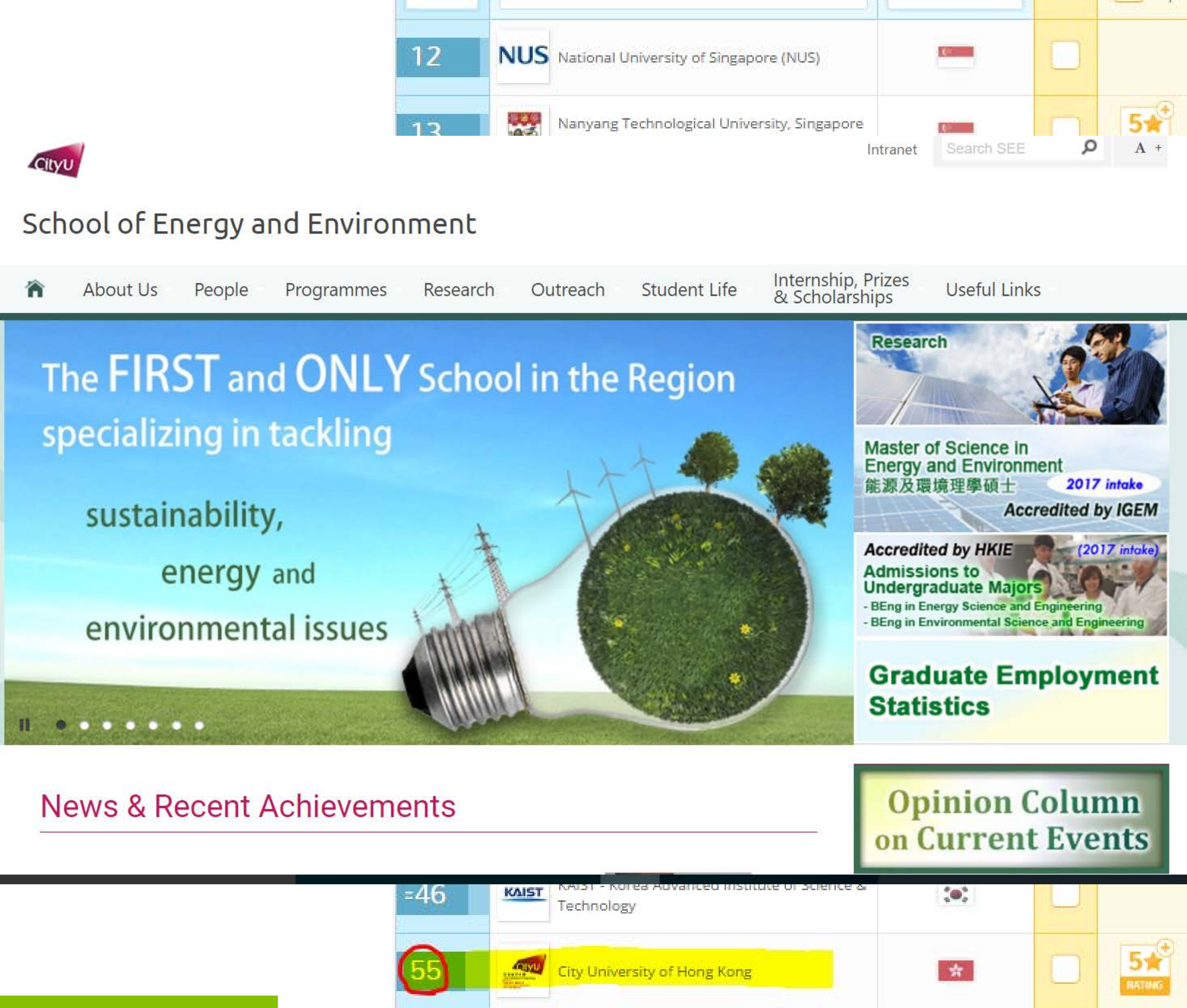
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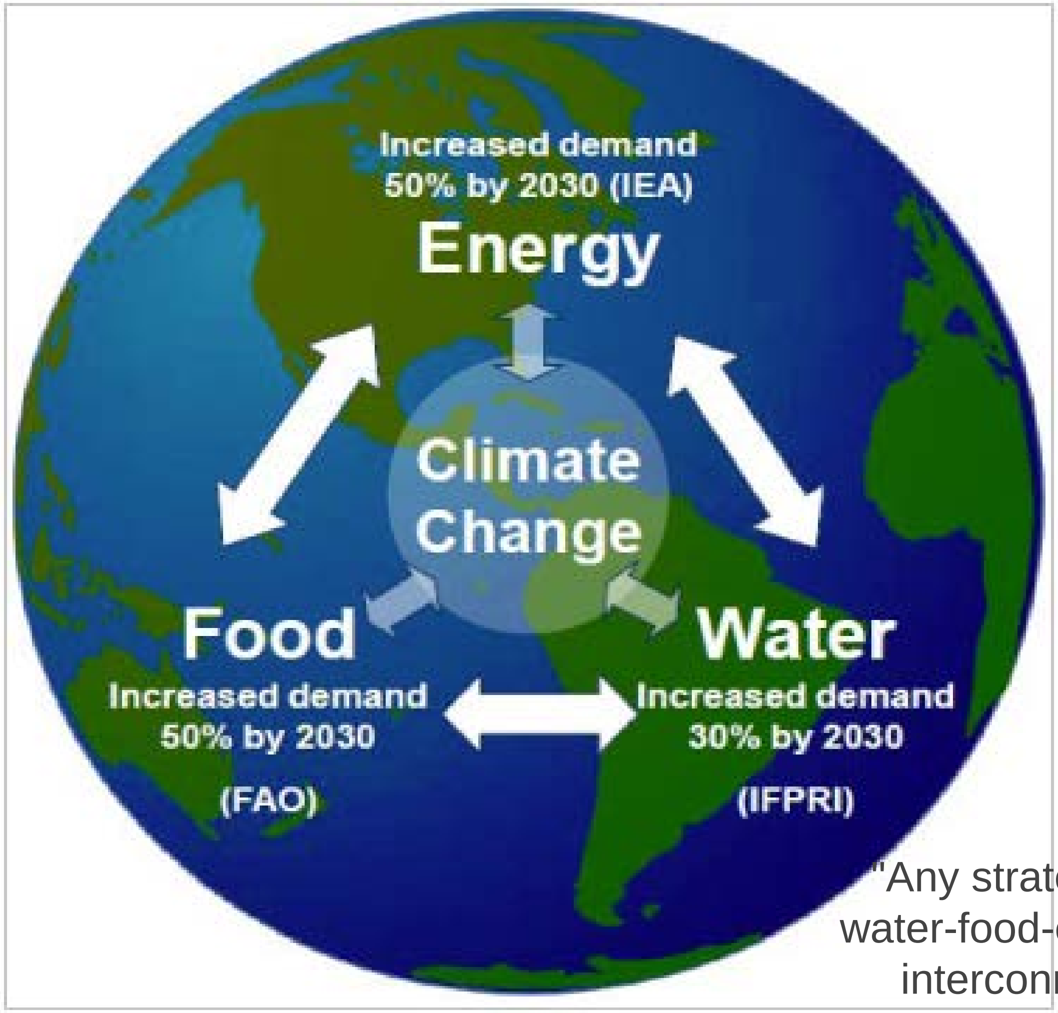
Water-Energy-Food Nexus



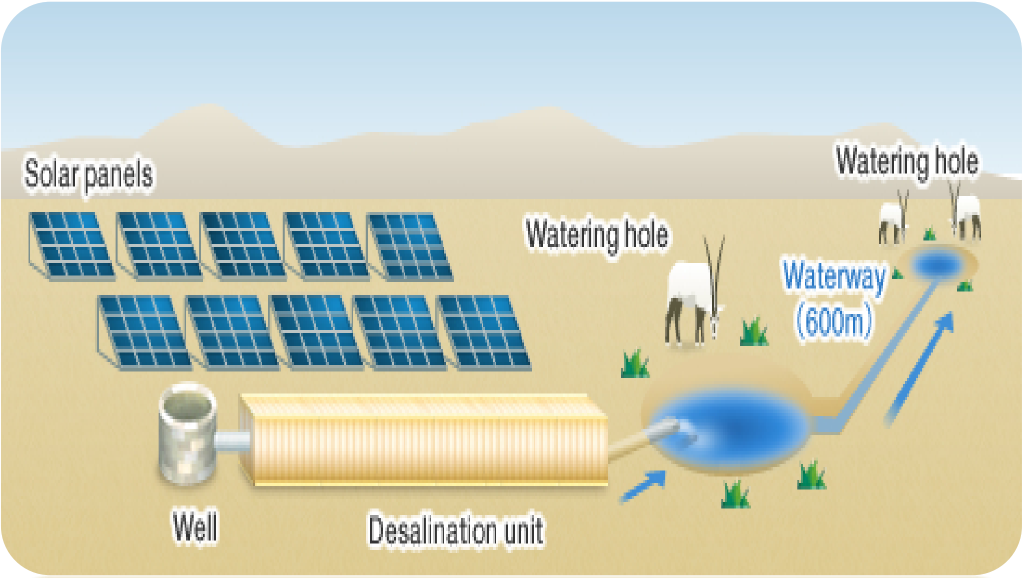
1. Where we can get additional water?

2. Membrane technology can be a sustainable?

"Any strategy that focuses on one part of the water-food-energy nexus without considering its interconnections risks serious unintended consequences."

World Economic Forum Global Risks Report 2011

❖ Water-Energy nexus Poly-generation Desalination



<Example: Hitachi group's solar-powered desalination technology (United Arab Emirates)>

✓ **Features**

: powered by renewable energy sources

(solar, geothermal, industrial waste heat..)

✓ **Advantages**

- **Poly-generation** (co-location, co-generation)
- **Low operating costs**, low infrastructure cost
- **Improvement** of process **efficiency**

Energy requirements (or cost) of seawater desalination

Process	Total Energy (kW-h/m3)	Capital Cost ($/m3/d)	Unit Water ($/m3)
Multi Stage Flash/MSF (without waste heat)	55-57		
MSF (with waste heat)	**10 - 16**	1000 - 1500	0.8 -1.0
Multi Effect Distillation/MED (w/o waste heat)	40-43		
MED (with waste heat)	6-9	900 - 1200	0.6-0.8
Sea Water Reverse Osmosis/ SWRO	3 - 6	800 - 1000	0.5-0.8
SWRO (with energy recovery)	**2 - 3**	**< 800**	**0.45 – 0.6**
Innovative Technologies/ Hybridization	**< 2.0 ***	**< 800**	**<0.5**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❖ Characteristics needed for membrane in for MD

- **Membrane characteristics for various types of membrane**

Commercial Membranes used for MD: polytetrafluroethylene (PTFE), Polyvinylidene fluoride (FVDF) and Polypropylene (PP)

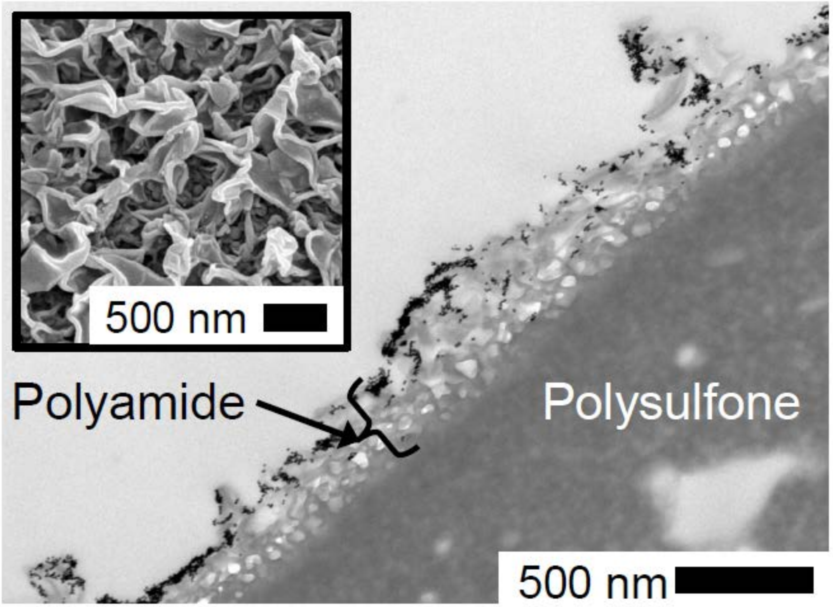
Membrane type	Manufacturer	Material	r_{av}(nm)	δ (μm)	LEP(kPa)	ε(%)
TF1000	Gelman	PTFE/PP	325	178	282	80
TF450	Gelman	PTFE/PP	235	178	138	80
TF200	Gelman	PTFE/PP	155	178	48	80
PV22	Millipore	PVDF	220	126±7	2.29±0.03	62±2
PV45	Millipore	PVDF	245	116±9	1.10±0.04	66±2
PTS20	Gore	PTFE/PP	200	184±8	4.63±8	44±6
PT20	Gore	PTFE/PP	200	64±5	3.68±0.01	90±1
PT45	Gore	PTFE/PP	450	77±8	2.88±0.01	89±4
HVHP	Millipore	PVDF	451.23	-	105	33.64
GVHP	Millipore	PVDF	265.53	-	204	32.74
Celgard X-20	Hoechst Celanese Co	PP	50	25	-	35

r_{av}: average pore size
δ: membrane thickness
LEP : liquid entry pressure
ε: membrane porosity

Source: Abdullah Alkhudhiri et al., 2012

Permeability-Selectivity Tradeoff→ how to overcome?

TFC polyamide is the **Gold Standard**, but prone to fouling



Elimelech, M. & Phillip W.A.
Science, 333, 2011, 712-717

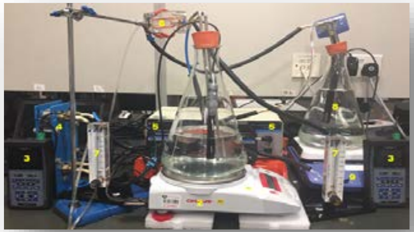
Need a **new paradigm** for surface modification, without reducing permeability and selectivity

Next Generation Membrane based Treatment Systems

- Good module
- High performance nano/molecule engineered membrane
- Low energy and chemical use
- Small footprint and capital costs
- High flux (water production)
- Recovery of valuable substances or chemicals
- Reliable and stable operation with less clearing and less susceptible for feed water characters and salinity

Introduction

MD Application

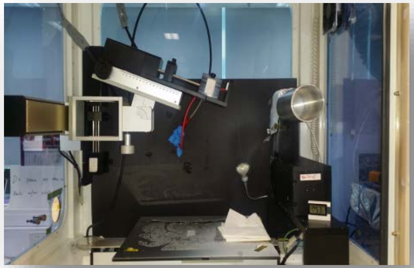


Wastewater treatment such as colored wastewater, oil-water separation and recovery of valuable component (fruit juices)

100% rejection ,lower operating temperatures, lower operating pressures and less requirements on membrane mechanical properties

Embryonic stage in terms of development due to membrane wetting and fouling issues that hinder the MD commercialization

Eletrospinning



Electrospinning: a simple and versatile method that can enhance the properties of the membrane by direct application of nanomaterials

Electrospun nanofibrous membranes (ENMs) have high porosity and hydrophobicity, which translates to high permeability and rejection

Poly(dimethylsiloxane) (PDMS), –Si(CH3)2O–, with high porosity and low surface energy can be consider as a hybrid composite material

Dye wastewater

Dyeing wastewater in large amounts and its treatment is riddled with complexities due to the inherent coloring and the multitude of chemicals

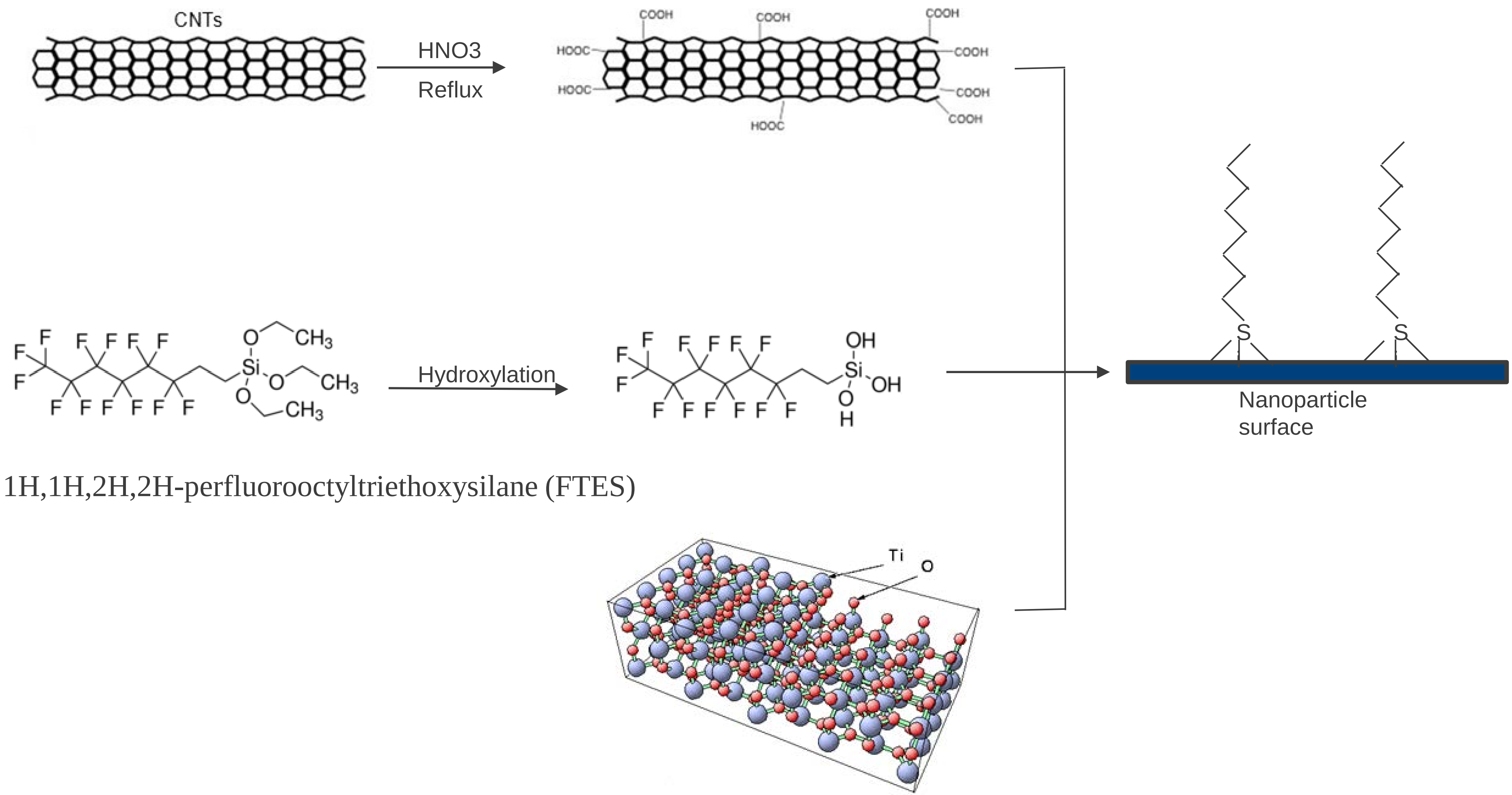
Developing an ideal membrane that is capable of color rejection as well as purification is essential.

Applied hybrid PDMS/PH membrane for treating dyeing wastewater (up to 200 mg L-1) of four different dyes by MD process

•**An, A.K.***; Guo, J.+; Jeong, S.; Lee, E. J.^; Tabatabai, S. A. A.; Leiknes, T. O. High flux and antifouling properties of negatively charged membrane for dyeing wastewater treatment by membrane distillation. ***Water Res.*** **2016**, *103*, 362–371.


Zero Liquid
Discharge

Next Generation, Highly Selective Desalination Membranes



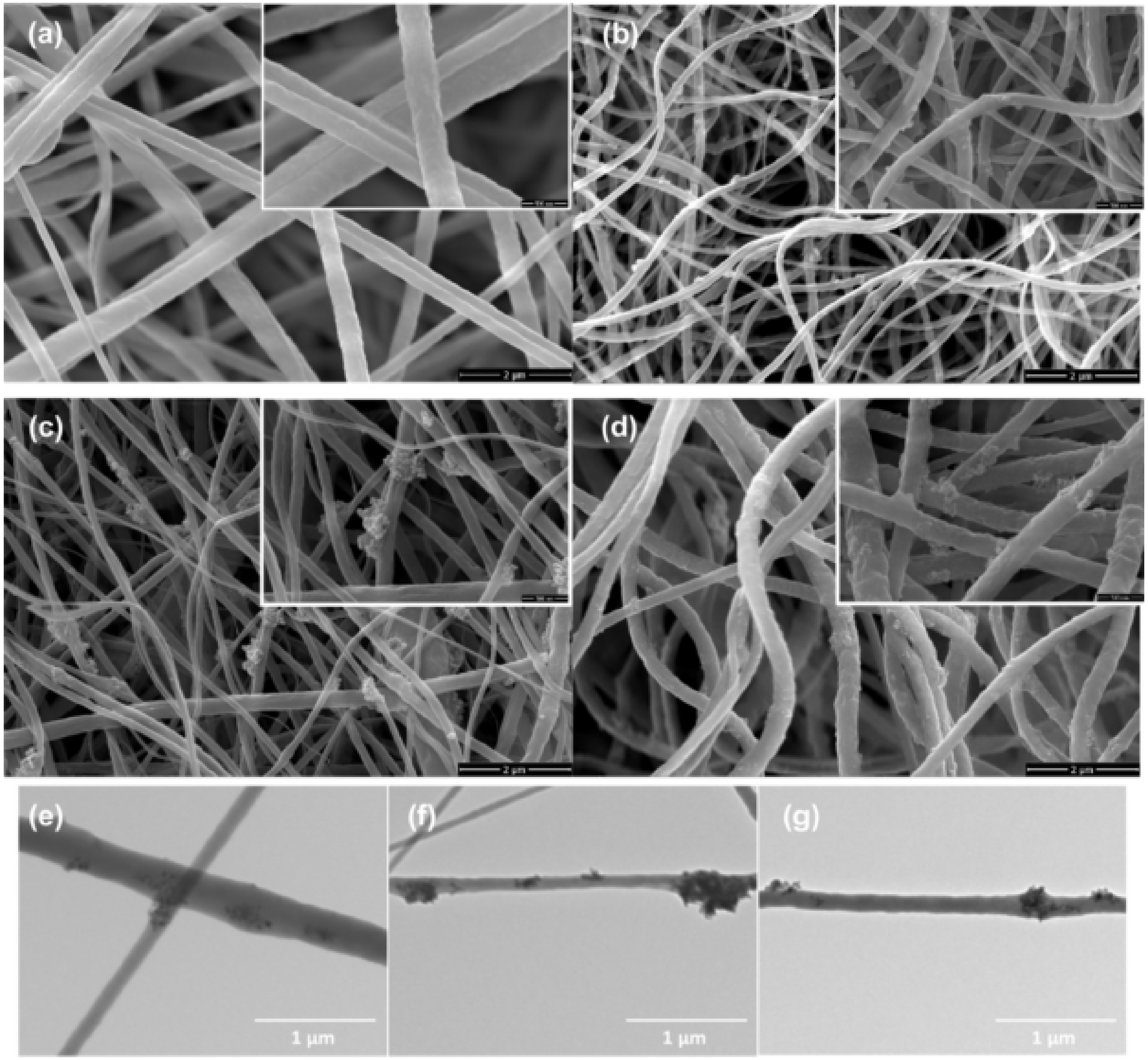
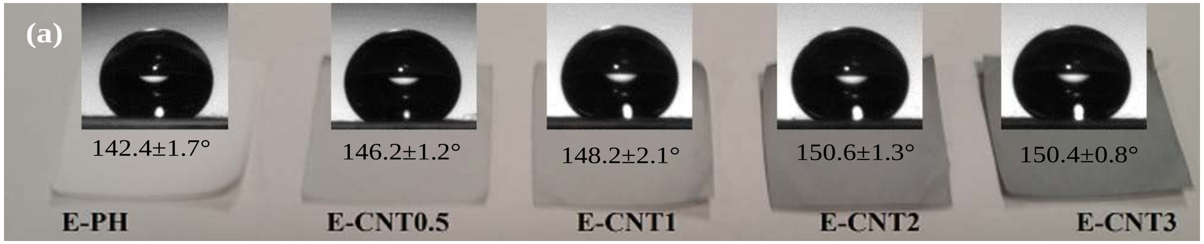
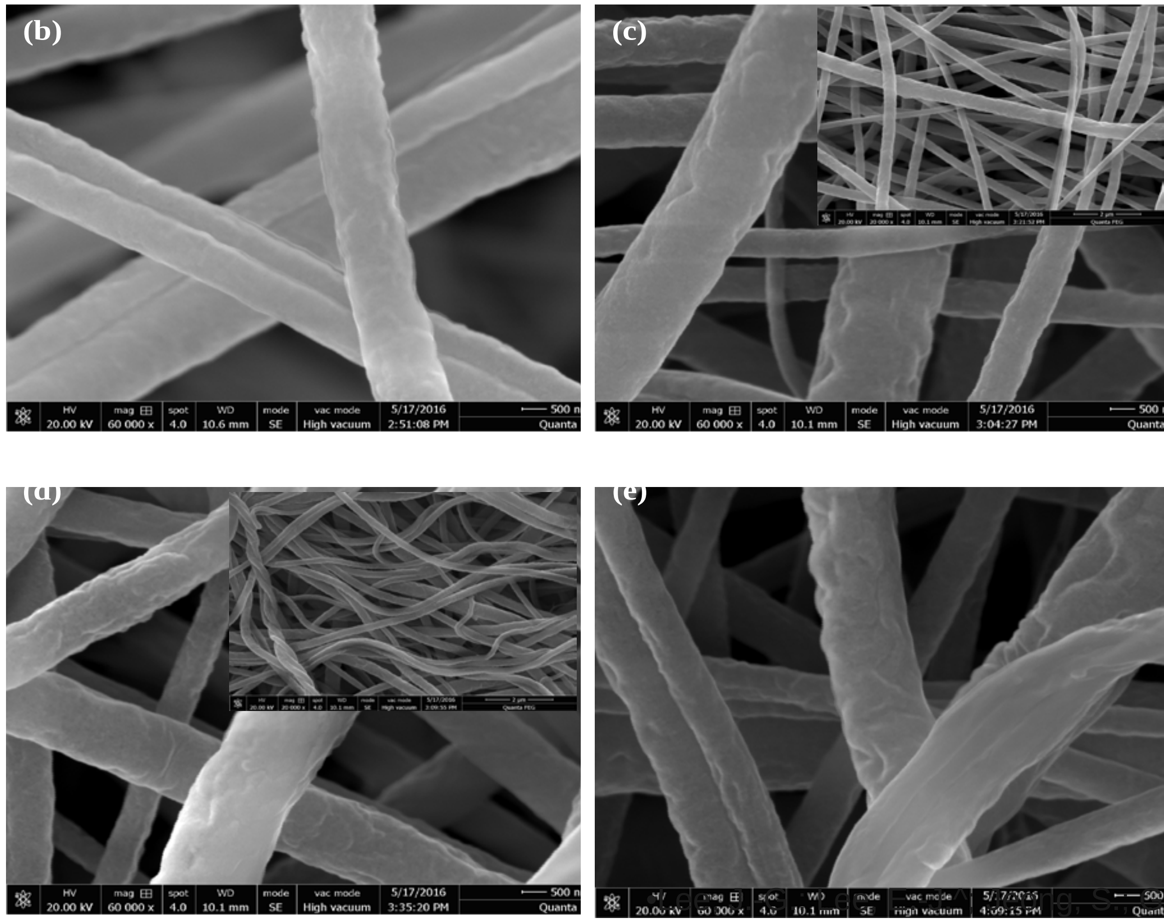


Fig. 5. FE-SEM images of (a) neat 20% PH ENM, (b) 10% PH ENM with 10% TiO_2, (c) 15% PH ENM with 10% TiO_2, and (d) 20% PH ENM with 10% TiO_2. TEM images of (e) 10% PH ENM with 10% TiO_2, (f) 15% PH ENM with 10% TiO_2, and (g) 20% PH ENM with 10% TiO_2.

E.-J. Lee, **A.K. An***, T. He, Y.C. Woo, H.K. Shon, Electrospun nanofiber membranes incorporating fluorosilane-coated **TiO2** nanocomposite for direct contact membrane distillation, **J. Memb. Sci.** 520 (2016) 145–154. doi:10.1016/j.memsci.2016.07.019.



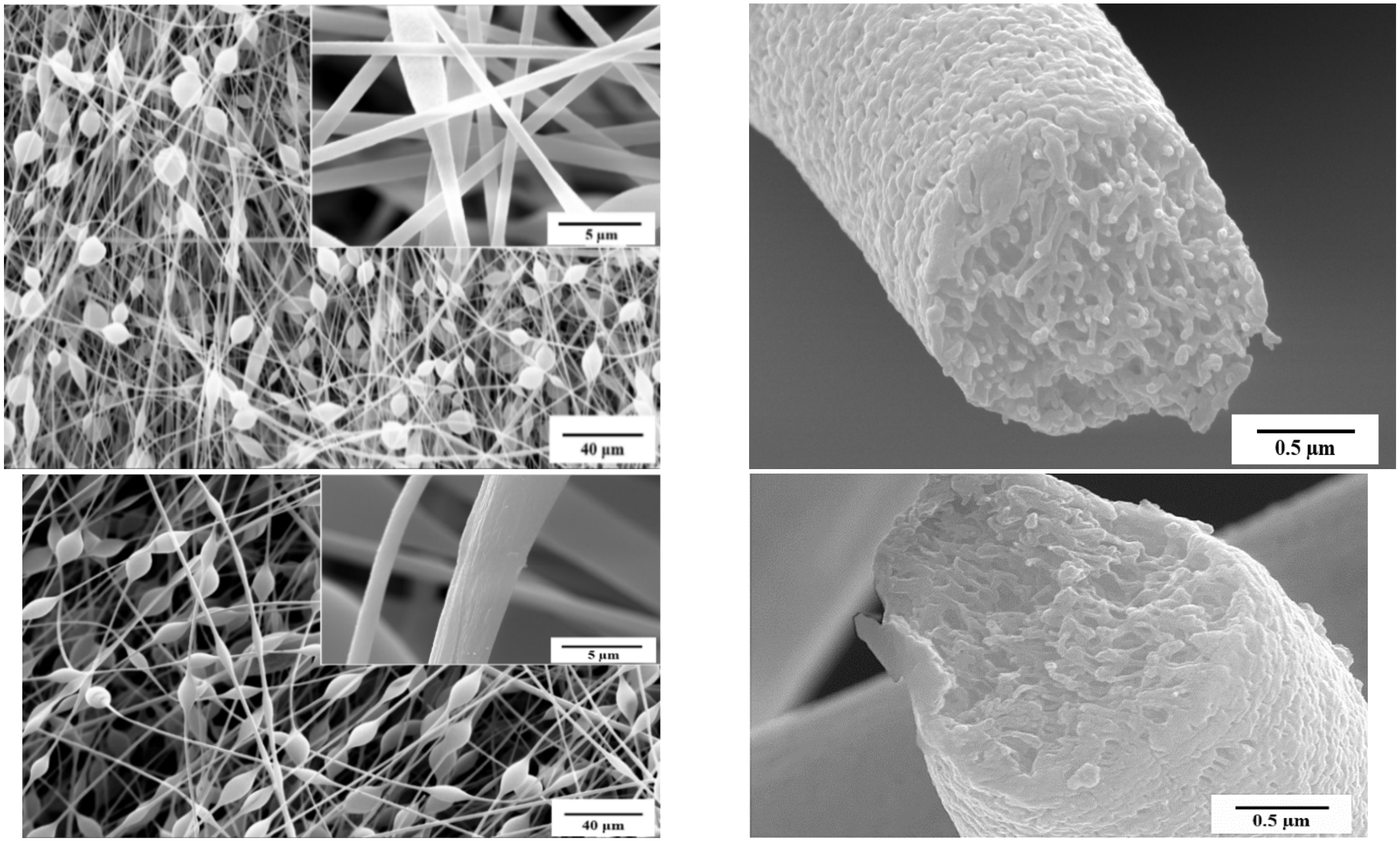
carbon nanotubes anchored into PVDF electrospun nanofibers



An, A.K.*; Lee, E.-J.^; Guo, J.+; Jeong, S.; Lee, J.-G.; Ghaffour, N.; Enhanced vapor transport in membrane distillation via functionalized carbon nanotubes anchored into electrospun nanofibres. ***Sci. Rep.*** **2017**, *7*, 41562. http://rdcu.be/oWCZ

Lee, J.-G.; Lee, E.-J.^; Jeong, S.; Guo, J.+; **An, A.K**.*.; Guo, H.; Kim, J.; Leiknes, T.; Ghaffour, N. Theoretical modeling and experimental validation of transport and separation properties of carbon nanotube electrospun membrane distillation. ***J. Memb. Sci.*** **2017**, *526*, 395–408.

CNTs reinforced super-hydrophobic-oleophilic electrospun polystyrene oil sorbent



SEM images of PS electrospun sorbents and fiber diameter distribution
Cross-sectional FE-SEM images of sorbents

Wu, J.+; **An, A.K.*;** Guo, J.+; Lee, E.-J.^; Farid, M. U.+; Jeong, S. CNTs reinforced super-hydrophobic-oleophilic electrospun polystyrene oil sorbent for enhanced sorption capacity and reusability. *Chem. Eng. J.* **2017,** *314*, 526-536

Without fluorine chemical can we reduce surface energy?

Methodology

-Fabrication of **Poly(dimethylsiloxane)** E-PDMS membrane

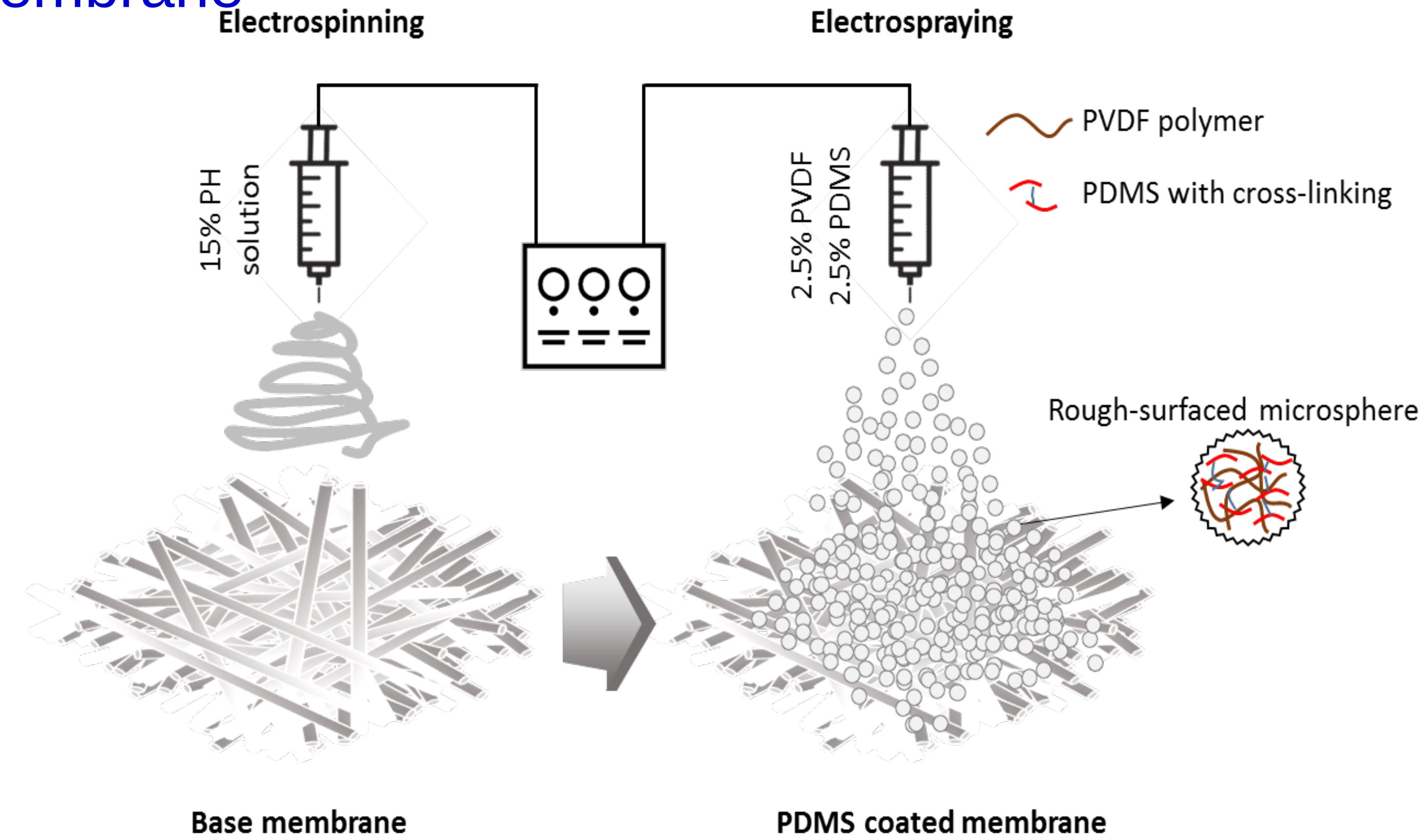
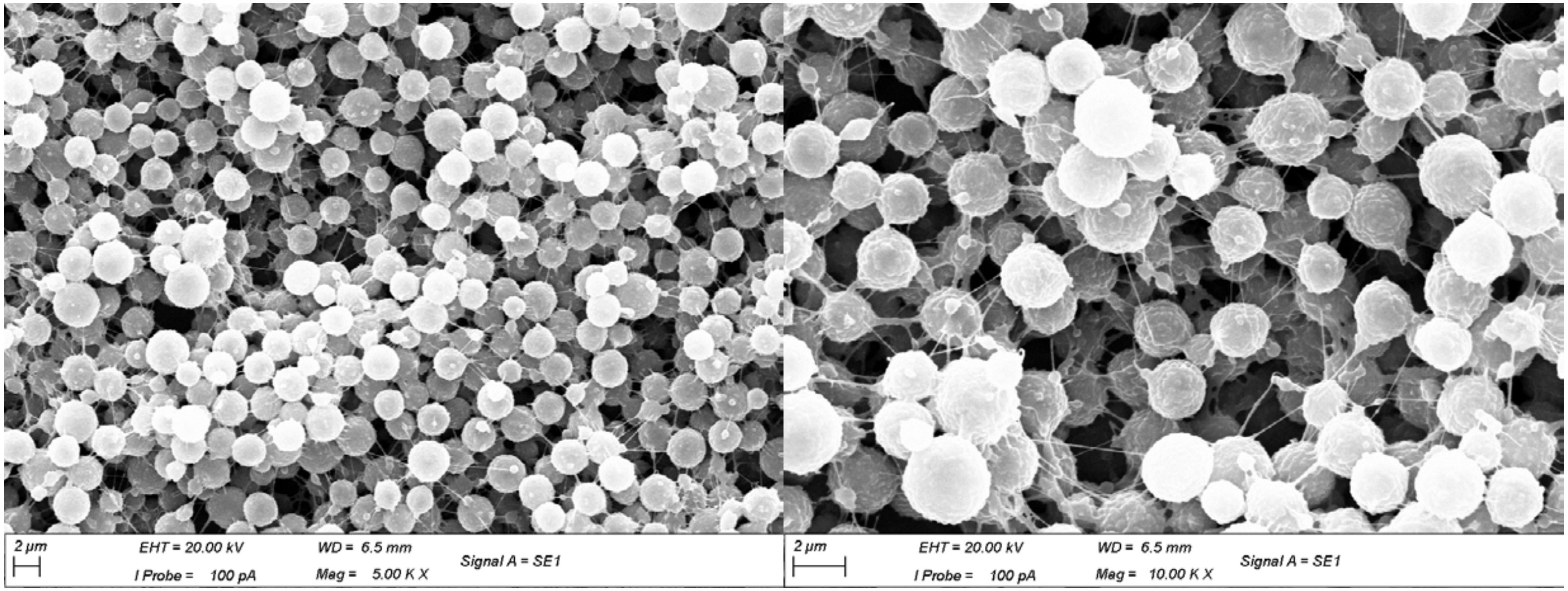


Figure 1. Schematic illustration of hybrid PDMS/PH membrane (E-PDMS) fabrication.

Poly(dimethylsiloxane) PDMS/PVDF hybrid electrospun membrane with superhydrophobic property and drop impact dynamics for dyeing wastewater treatment using membrane distillation



A.K. An, J. Guo, E.-J. Lee, S. Jeong, Y. Zhao, Z. Wang, T. Leiknes, PDMS/PVDF hybrid electrospun membrane with superhydrophobic property and drop impact dynamics for dyeing wastewater treatment using membrane distillation, **J. Memb. Sci.** (2016). doi:10.1016/j.memsci.2016.10.028.

Characteristics of E-PDMS membrane
-Droplet bouncing on the superhydrophobic surface

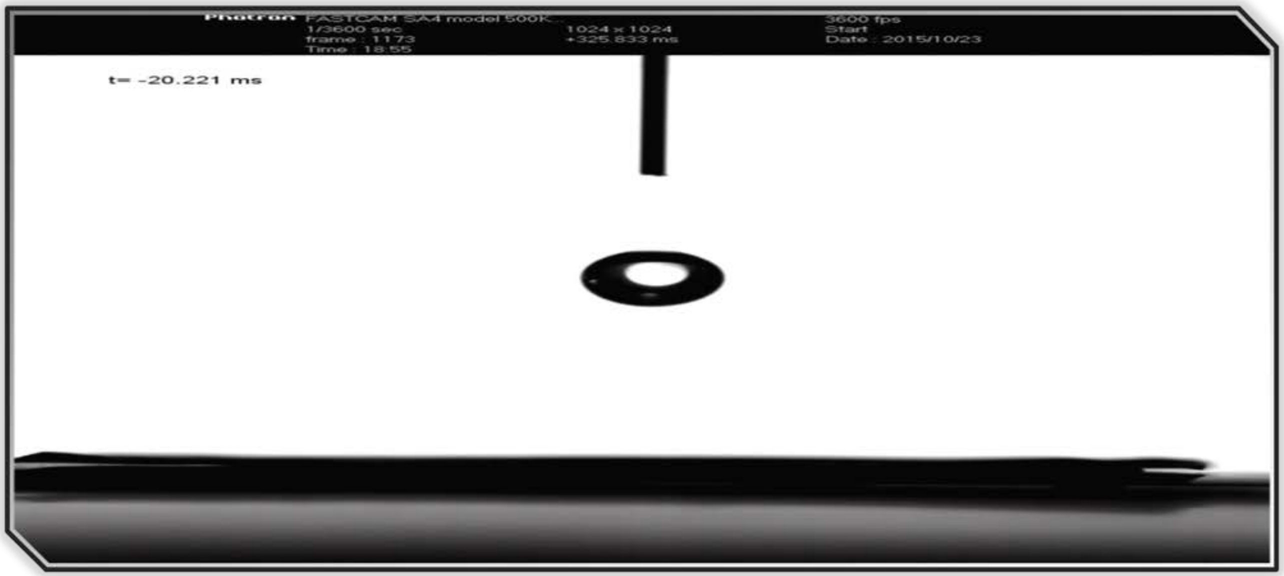


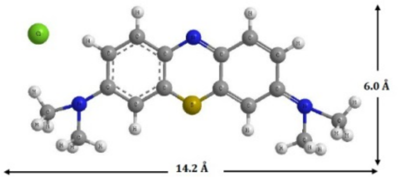
Figure 6. Superhydrophobic-like drop impact dynamics on the superhydrophobic surface of E-PDMS membrane: The selected snapshots show the complete rebounding of the droplet after impact on the hybrid superhydrophobic interface.

Methodology
-Membrane and Dyes

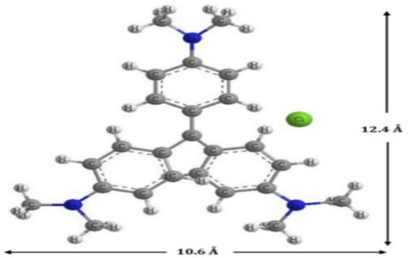
Table 1. Characteristics of the membranes used in this study.

Parameter	C-PVDF Commercial	E-PH Electrospinning	E-PDMS PDMS on E-PH
Material	PVDF	PH	PDMS/PH
Mean pore size (µm)	0.45	0.52	0.49
Porosity (%)	72.11	87.28	87.84
Membrane thickness (µm)	105	98	102
CA of water (º)	118.3	137.2	155.4
LEP* of water (bar)	1.17	0.92	1.26
Pure water flux** (LMH)	25.2	36.2	37.6

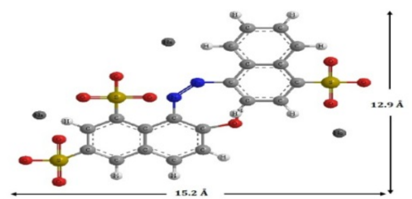
* LEP: liquid entry pressure. ** Pure water flux was measured in DCMD at 0.5 L min^{-1} of flow rate. Temperatures of feed and permeate were 60 ºC and 20 ºC, respectively.



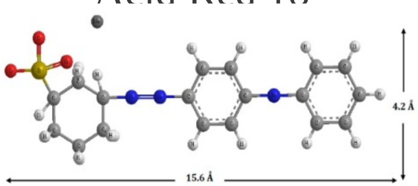
Methylene Blue



Crystal Violet



Acid Red 18



Acid Yellow 36

Methodology
-DCMD set-up

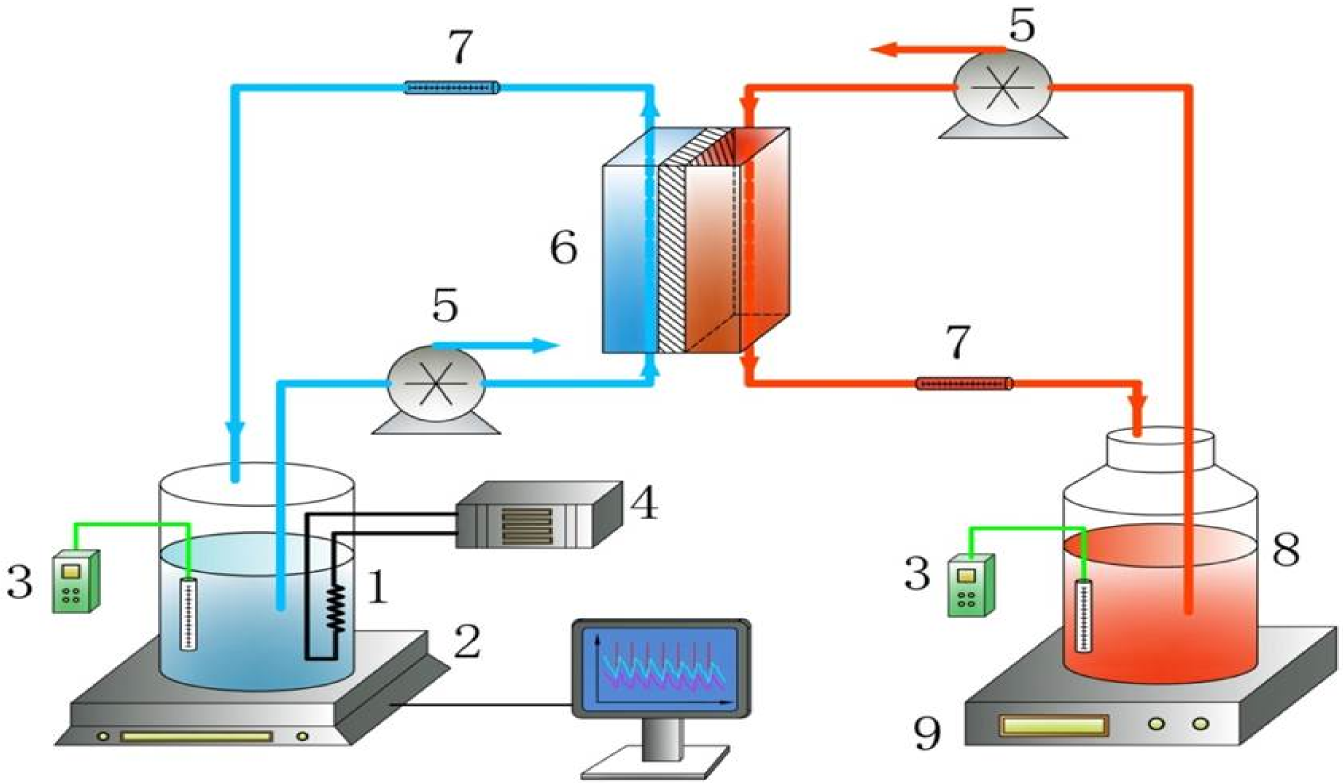


Figure 2. Schematic diagram of the DCMD test unit (1: Permeate tank, 2: Digital balance connected to a computer, 3: Thermometers, 4: Cooling unit, 5: Pumps, 6: Flat sheet membrane module, 7: Flow meters, 8: Feed reservoir, 9: Hotplate).

Characteristics of E-PDMS membrane
-Morphology and Chemical structure

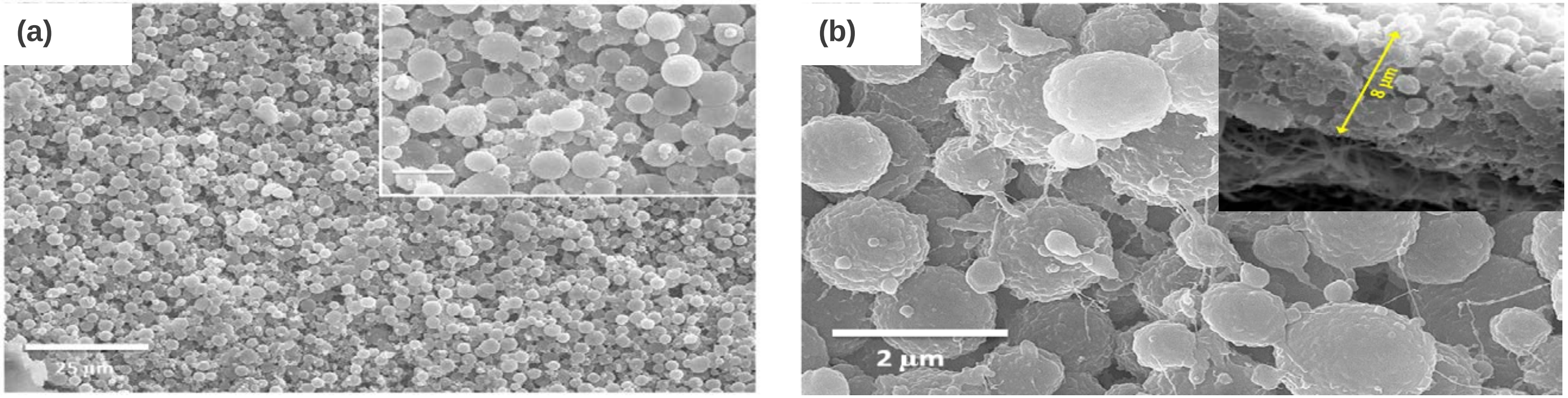


Figure 3. SEM images of the of E-PDMS membrane laboratory-fabricated (top right of b: cross-sectional SEM image).

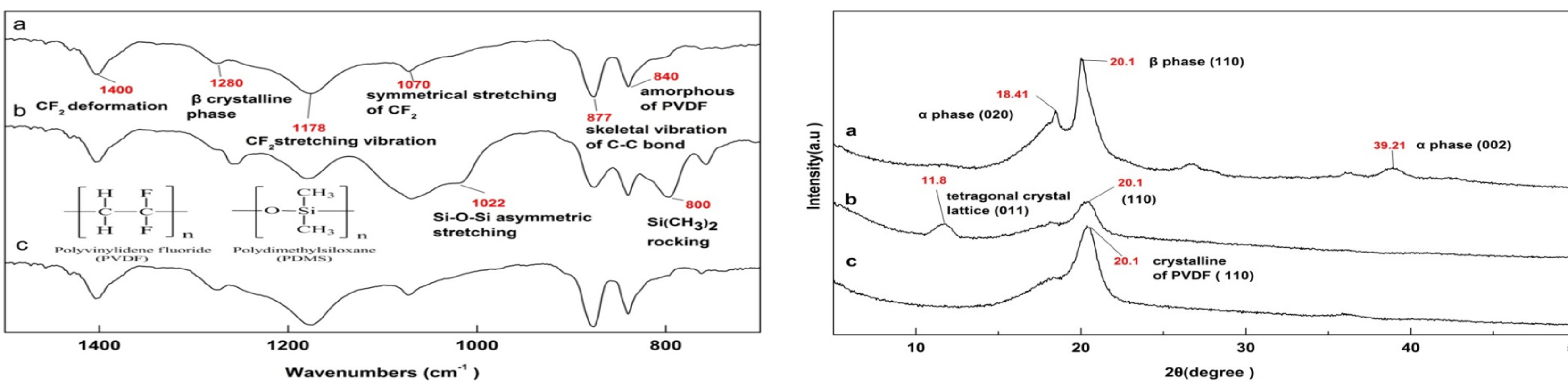


Figure 4 (A). FTIR of (a) the C-PVDF membrane, (b) the feed side of and (c) the permeate side of E-PDMS membrane ; and (B). XRD of (a) C-PVDF, (b) E-PDMS and (c) E-PH membranes.

Characteristics of E-PDMS membrane
-Hydrophobicity and surface roughness

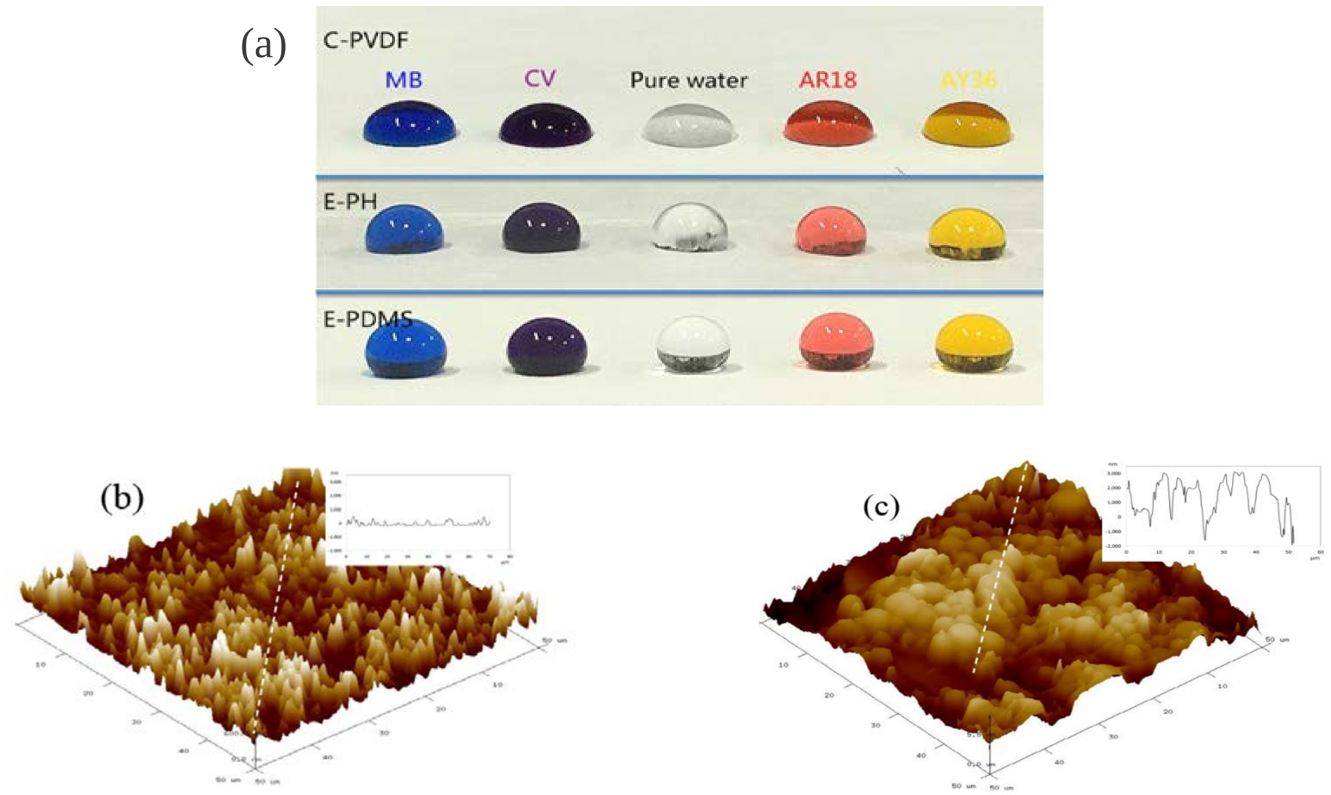


Figure 5. (a) Pure water and dye droplets on the surfaces of the three different membranes (C-PVDF, E-PH and E-PDMS) and (b) C-PVDF and (c) E-PDMS membranes' roughness analyzed using AFM.

Characteristics of E-PDMS membrane
-Surface zeta potential

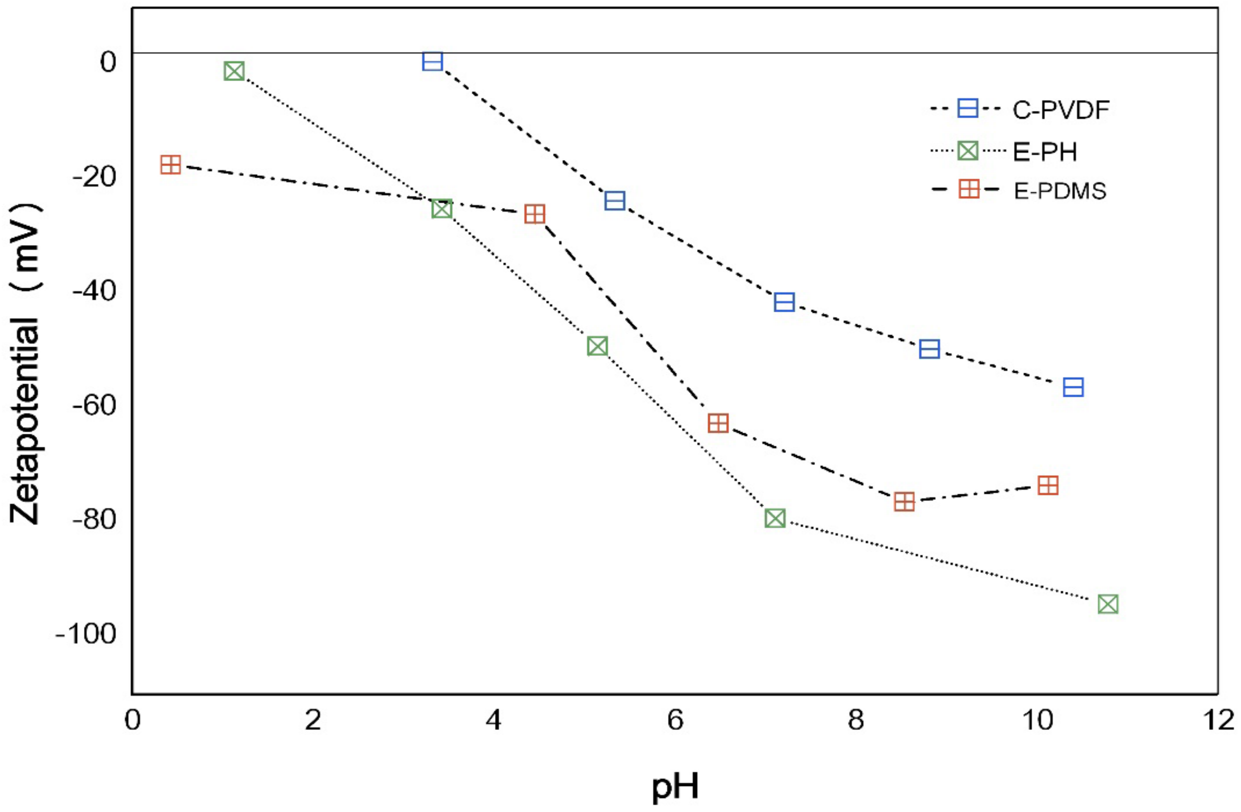


Figure 7. Zeta potentials of the membranes (C-PVDF, E-PH and E-PDMS) as a function of pH.

MD performance in treating synthetic dye solution
-MD water flux

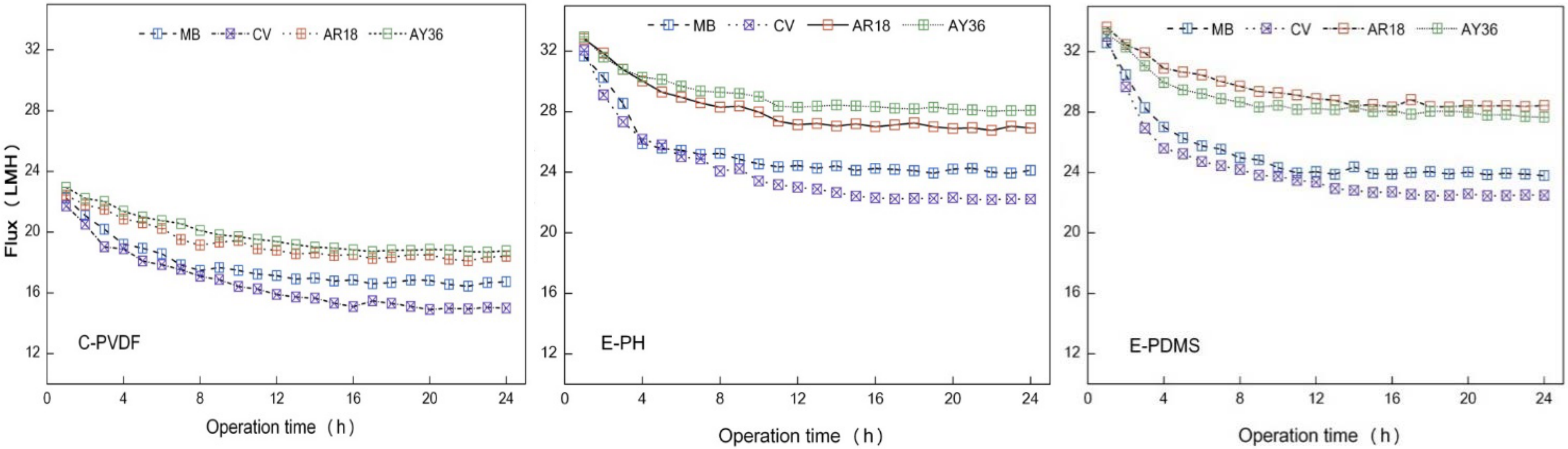


Figure 8. Water flux as a function of MD operation time for the treatment of four different dyes using three different membranes (C-PVDF, E-PH, and E-PDMS) (feed temperature = 60 °C, flow rate = 0.5 L min^{-1}, and C_0 = 100 mg L^{-1}).

MD performance in treating synthetic dye solution
-Dye rejection

Table 2. Initial fluxes, average fluxes, and color removal efficiencies in DCMD operation using three membranes in treating four different dyes during 24h.

Membrane	**Dye**	**MB**	**CV**	**AR18**	**AY36**
C-PVDF	Initial flux (LMH)	3.24 ±0.58	22.17 ±1.09	22.44 ±0.22	22.95 ±0.68
	Ave. flux (LMH)	17.75 ±1.24	16.61 ±0.96	19.31 ±1.33	19.82 ±1.82
	Color removal (%)	98.29 ±0.42	96.54 ±0.37	100	100
E-PH	Initial flux (LMH)	31.67 ±0.29	32.06 ±0.57	32.79 ±0.43	32.93 ±0.71
	Ave. flux (LMH)	25.24 ±1.47	24.02 ±0.87	28.16 ±1.02	29.06 ±0.74
	Color removal (%)	98.74 ±0.31	97.62 ±0.92	100	100
E-PDMS	Initial flux (LMH)	32.58 ±0.59	33.02 ±0.26	33.63 ±0.46	33.19 ±0.81
	Ave. flux (LMH)	25.23 ±1.62	24.14 ±1.35	29.5 ±1.04	28.81 ±1.11
	Color removal (%)	100	100	100	100

MD performance in treating synthetic dye solution
-Fouling issue and dye adsorption

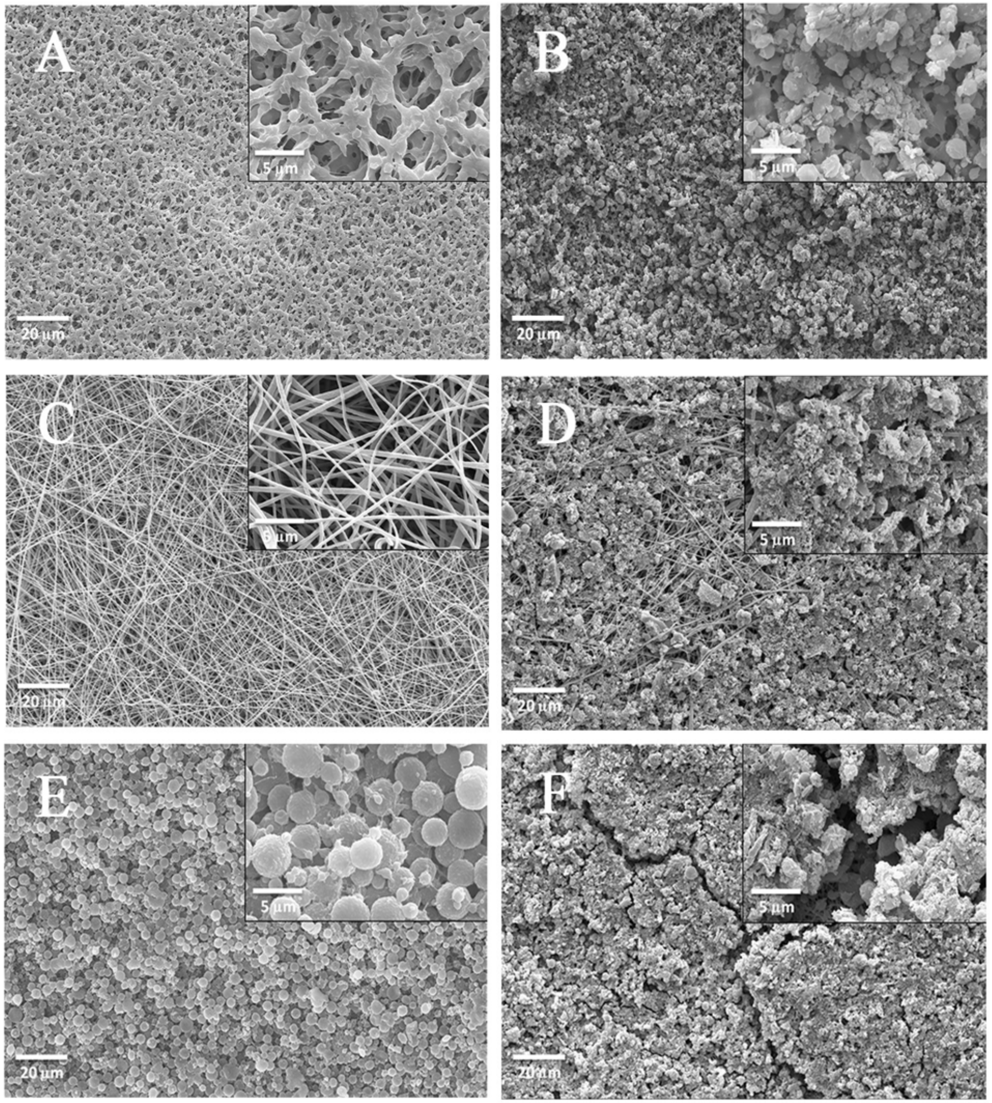


Figure. 9 SEM images (X2,000 and X15,000) of (a) the virgin C-PVDF membrane, (b) the C-PVDF membrane after MD, (c) the virgin E-PH membrane, (d) the E-PH membrane after MD, (e) the virgin E-PDMS membrane, and (f) the E-PDMS membrane after MD in CV treatment.

Anti-fouling property of superhydrophobic surface
-Membrane cleaning with simple water flushing

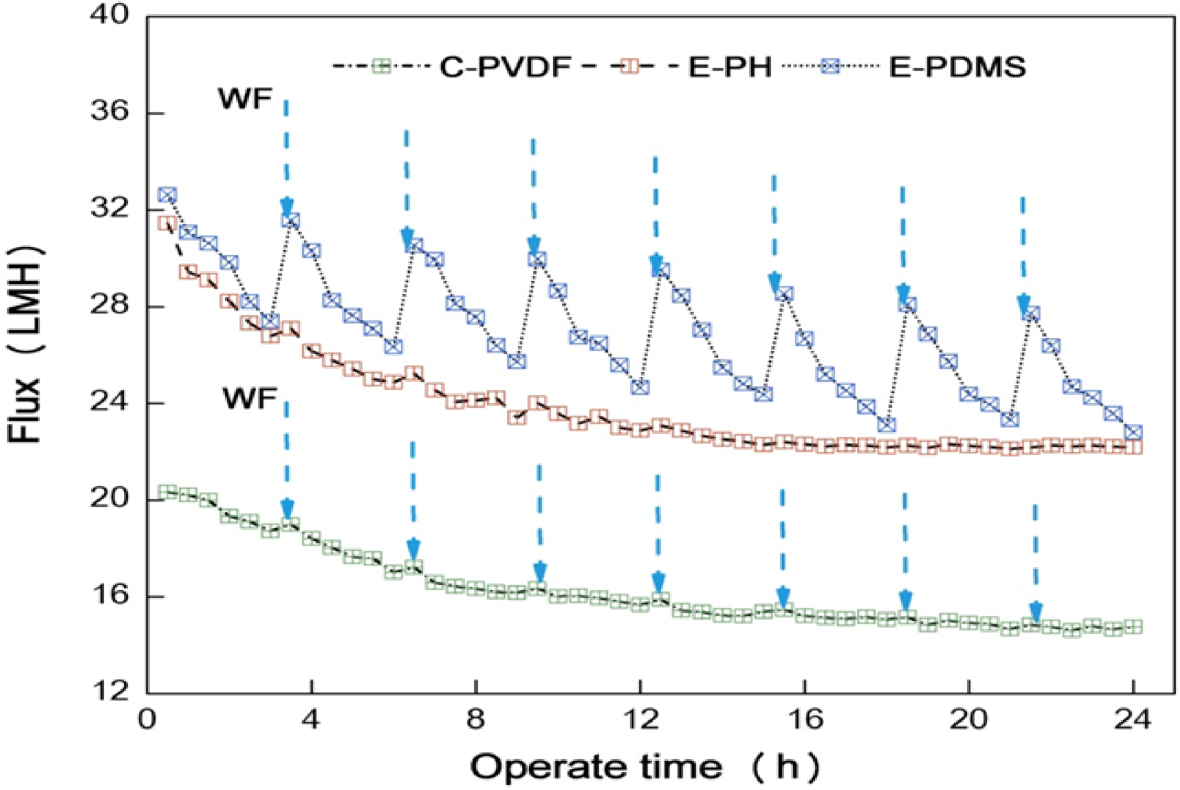


Figure 10. Water flux as a function of MD operation time for C-PVDF, E-PF and E-PDMS membranes for CV treatment (C0 = 100 mg L-1). WF was conducted for 10 min every 3 h at 0.5 L min-1 of flow rate.

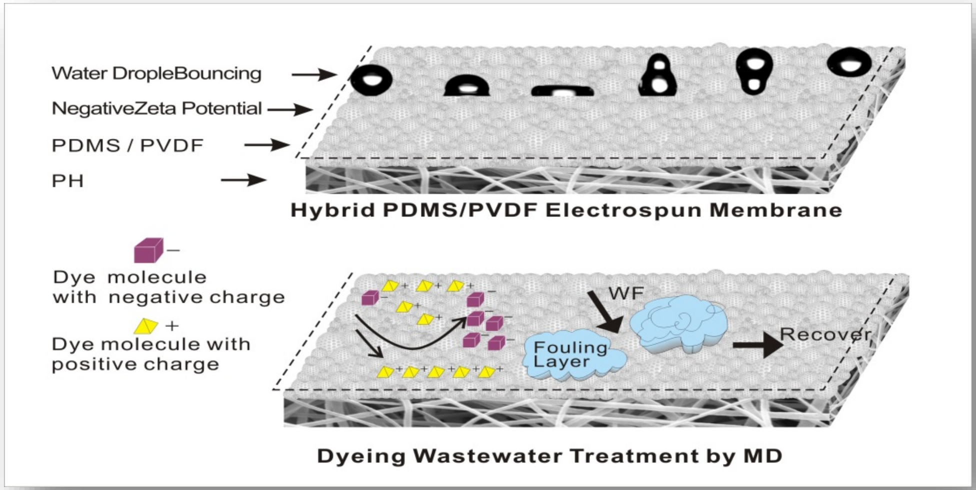
Anti-fouling property of superhydrophobic surface
- E-PDMS membrane regeneration

Figure 11. Behavior of a water droplet on the surface of the E-PDMS membrane (a) virgin membrane, (b) after 24 h of MD operation, at which point the CA dropped from 155.4 to 87.1°, and (c) after WF for 10 min, in this case the CA was 99% recovered to 154.9°.

Figure 12. The surface picture of (a) C-PVDF and (b) E-PDMS membranes after 24 h MD operation with WF for CV treatment.

Conclusion

- PDMS were successfully coated on the E-PH membrane via electrospinning with superhydrophobicity and high roughness
- Sulfonate groups of the dyes were easily repelled by the highly negative zeta potential of E-PDMS membrane.
- Higher hydrophobicity of membrane formed a stronger repulsive force and form of a dye–dye structure between dye and the membrane.
- The droplet bouncing effect of the E-PDMS membrane minimized the contact of dyes with the membrane.
- Superhydrophobic E-PDMS membrane affected the fouling mechanism to form loose fouling structures to be easily washed out by simply WF.



Thank you and hope to see you in Hong Kong!