



Historical Perspective

Recent advances in membrane development for treating surfactant- and oil-containing feed streams via membrane distillation

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ARTICLE INFO

Article history:

18 August 2019

Available online 28 August 2019

Keywords:

Membrane distillation
 Janus membrane
 Omniphobic membrane
 Low-surface-tension
 Re-entrant structure

ABSTRACT

Membrane distillation (MD) has been touted as a promising technology for niche applications such as desalination of surfactant- and oil-containing feed streams. Hitherto, the deployment of conventional hydrophobic MD membranes for such applications is limited and unsatisfactory. This is because the presence of surfactants and oils in aqueous feed streams reduces the surface-tension of these media significantly and the attachment of these contaminants onto hydrophobic membrane surfaces often leads to membrane fouling and pore wetting, which compromises on the quantity and quality of water recovered. Endowing MD membranes with surfaces of special wettabilities has been proposed as a strategy to combat membrane fouling and pore wetting. This involves the design of local kinetic energy barriers such as multilevel re-entrant surface structures, surfaces with ultralow surface-energies, and interfacial hydration layers to impede transition to the fully-wetted Wenzel state. This review critiques the state-of-the-art fabrication and surface-modification methods as well as practices used in the development of omniphobic and Janus MD membranes with specific emphasis on the advances, challenges, and future improvements for application in challenging surfactant- and oil-containing feed streams.

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1. Introduction

Membrane distillation (MD) is an emerging separation process driven by the partial vapor difference arising from the temperature

gradient across a hydrophobic porous membrane [1–3]. There are four main configurations for the MD process, namely direct-contact membrane distillation (DCMD), vacuum membrane distillation (VMD), sweeping gas membrane distillation (SGMD), and air gap membrane distillation (AGMD), all of which involve coupled mass and heat transfer phenomena. Most of the papers published in the literature have focused on the DCMD configuration, which contributes to >60% of the papers published, because of its simple operation mode [4]. In the DCMD process as shown in Fig. 1, an aqueous solution (usually deionized water)

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Nomenclature

θ	Equilibrium contact angle
θ^*	Apparent contact angle
ψ	Local geometric angle
AGMD	Air gap membrane distillation
AgNP	Silver nanoparticles
APTES	(3-Aminopropyl)triethoxysilane
ATRP	Atom-transfer radical-polymerization
BTEAC	Benzyltriethylammonium chloride
CA	Cellulose acetate
CBD	Chemical bath deposition
CF ₄	Tetrafluoromethane
CMC	Critical micelle concentration
CTAB	Cetyltrimethylammonium bromide
CTS	Chitosan
DCMD	Direct-contact membrane distillation
DTAB	Dodecyltrimethylammonium bromide
EDA	Ethanediamine
f_1	Area fraction of solid-liquid interface
f_2	Area fraction of liquid-air interface
FAS	1H,1H,2H,2H-Perfluorodecyltrimethoxysilane
FAS17	1H,1H,2H,2H-Perfluorodecyltriethoxysilane
FDTS	(heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane
FESEM	Field emission scanning electron microscopy
F-POSS	Fluorinated-decyl polyhedraloligomeric silsesquioxane
FS	Fluorosurfactant
FTCS	Fluorododecyltrichlorosilane
GA	Glutaraldehyde
GO	Graphene oxide
HLB	Hydrophilic-lipophilic balance
LBL	Layer-by-layer
LCA	Liquid contact angle
LEP	Liquid entry pressure
MD	Membrane distillation
N.A.	Not applicable
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NIPS	Non-solvent induced phase separation
O/W	Oil-in-water emulsion
PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile
PDA	Polydopamine
PDDA	Poly(diallyldimethylammonium chloride)
PEG	Polyethylene glycol
PEI	Polyethylenimine
PFO	Perfluorooctanoate
PFTS	1H,1H,2H,2H-perfluorooctyl trichlorosilane
PS	Polystyrene
PVA	Polyvinyl alcohol
PVDF	Poly(vinylidene fluoride)
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
PTFE	Polytetrafluoroethylene
r	Roughness ratio
SBMA	[2-(Methacryloyloxy)-ethyl]dimethyl-(3-sulfopropyl) ammonium hydroxide
SDBS	Sodium dodecyl benzene sulfonate
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
SGMD	Sweeping gas membrane distillation
SiA	Silica aerogel
SiNP	Silica nanoparticles
TEM	Transmission electron microscopy

Tween® 20	Polyoxyethylenesorbitan monooleate
Tween® 80	Polyoxyethylenesorbitan monooleate
T_f	Feed temperature
T_p	Permeate temperature
VMD	Vacuum membrane distillation
ZnO	Zinc oxide

that is colder than the feed is in direct contact with the permeate side of the membrane. The membrane acts as a selective barrier that allows only vapor molecules from the heated feed stream to percolate through the hydrophobic membrane pores, and condense into purified distillate upon contact with the cold permeate stream on the other side of the membrane. Despite being able to theoretically reject all non-volatile solutes (i.e. salts), the main drawback of the MD process is the large amount of energy that is consumed during the liquid-vapor phase change process, which coupled with incomplete recovery of the latent heat render the MD process energy-inefficient as a standalone system [5]. Nevertheless, MD's ability to leverage low-grade waste heat as an energy source while operating at a low pressure and its negligible sensitivity to varying feed salinity merit consideration over conventional pressure-driven membrane processes for its application in water recovery from high-salinity feed streams such as brines from produced water [6–10]. This is because the high osmotic pressure (up to 360,000 mg L⁻¹) of these wastewaters would have rendered the application of conventional pressure-driven membrane processes (salinity limit of 70,000 mg L⁻¹) inadequate [11,12].

Fig. 2 shows the different types of MD membrane that have been developed over the years. In its infancy, the predominant application of the MD process was desalting, and the most commonly used membranes were originally fabricated for microfiltration or ultrafiltration purposes [13]. As the technology advanced, dedicated membranes with hydrophobic and superhydrophobic properties were developed for sustainable MD operations in relatively clean waters [1,2,14–16]. Often, hydrophobic materials are considered to have water contact angle values of >90° whereas superhydrophobic materials have water contact angle values of >150° and/or contact angle hysteresis of <10° [17]. However, as researchers began to venture into niche industries such as the oil and gas industry, it was realized that further development of bespoke membranes was of paramount importance. This is because while surfactants and oils can sometimes be found in other high-salinity waste streams, they are ubiquitous in oil field and shale

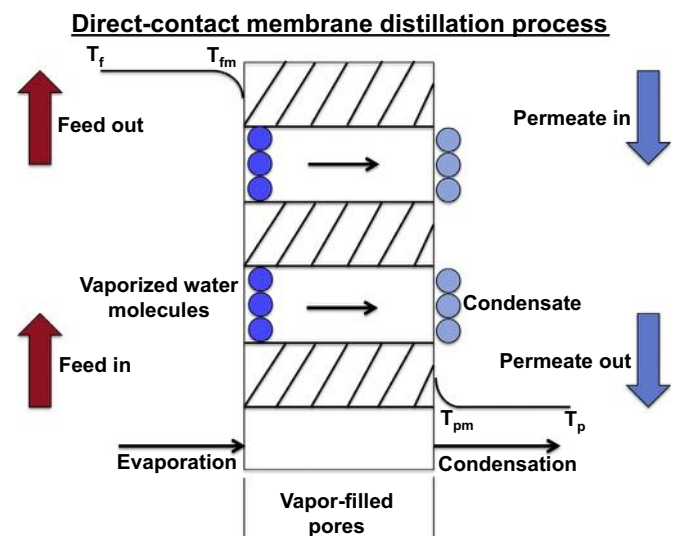


Fig. 1. Schematic of the DCMD process.

gas produced water and pose significant challenges to the applicability of the MD process [18].

Surfactants, a blend of surface-active agents, are amphiphilic substances consisting of lyophilic/hydrophilic head-groups that have an affinity for polar media (water-soluble) and lyophobic/hydrophobic tails that have an affinity for non-polar media (water-insoluble or oil-soluble). They are classified according to their polar head-groups: non-ionic, anionic, cationic, and zwitterionic [19]. Even at low concentrations, surfactants can adsorb onto surfaces or assemble at interfaces, and in turn reduce the surface- or interfacial-tension of a medium significantly. Today, surfactants are used extensively as the basic constituents of a variety of products that include detergents, paints, dyes, cosmetics, pharmaceuticals, pesticides, fibers, and plastics to name a few [20]. On the other hand, oils are low-surface-tension contaminants that are hydrophobic in nature. They are released into the environment on a large scale due to the rapid development of oil-related industries such as the petroleum, food, textile, leather, steel, and metal-finishing industries [21]. The deployment of conventional MD membranes for the treatment of low-surface-tension high-salinity waste streams is undesirable and hence limited since surfactant unimers and oil droplets have the tendency to readily adsorb and accumulate on the hydrophobic/superhydrophobic surfaces of these membranes, which in turn reduce the hydrophobicity and liquid entry pressure (LEP) of membrane pores and accelerate membrane wetting [22–25]. In view of that, customized membranes with special wettabilities such as omniphobic and Janus membranes are required to circumvent the issues of fouling and wetting that would otherwise be encountered in low-surface-tension feed streams if conventional MD membranes were used.

While the influences of pretreatment and operating conditions have been intensively studied, there have been very few detailed reports available in the literature hitherto on the influences of surfactants and oils on membrane performances in MD applications. This in turn has discouraged the use of MD for niche applications. In a first-of-its-kind study, Chew et al. presented fundamental understanding of the relationship between different low-surface-tension media (oil solutions, surfactant solutions, and surfactant-stabilized oil-in-water (O/W) emulsions) and commercial hydrophobic poly(vinylidene fluoride) (PVDF) membrane surfaces [22]. The results reveal that the onset of wetting was primarily dependent on the hydrophilic-lipophilic balance (HLB) value and critical micelle concentration (CMC) of surfactants. Notably, the

presence of oil in O/W emulsions delayed the occurrence of membrane wetting. In a separate study conducted by Han et al., it was discovered that both salt and surfactant were the primary contributors to poor membrane performances, causing serious fouling and wetting issues [26]. Wen et al. verified that the increment in salt concentration could delay the onset of wetting [27]. Recently, researchers have also attempted to better understand the mechanisms involved in membrane wetting caused by surfactants and oils via electrical impedance spectroscopy [28,29], molecular dynamics simulations [30], and theoretical models [31]. With a more solid foundation built upon these studies, robust MD membranes with fouling- and wetting-resistant properties could be engineered via targeted surface-modification techniques for water recovery from low-surface-tension high-salinity feed streams.

While there have been recent reviews focusing on the fouling [32] and wetting [33] phenomena in MD as well as various synthesis methods of MD membranes for relatively clean waters [34], no comprehensive literature review has delved into state-of-the-art membrane development techniques dedicated to surfactant- and oil-containing waste streams. Furthermore, existing reviews on the development of membranes for oily wastewater treatment have predominantly focused on pressure-driven membrane processes [35]. This article presents a critical review on the subject for the MD domain. The aim of this paper is to lay the groundwork for further improvements in membrane development and its subsequent practical implementation for niche MD applications.

2. Mechanisms of membrane fouling and wetting in surfactant- and oil-containing feed streams

The accumulation of surfactant unimers on a hydrophobic porous membrane surface is a non-cooperative binding process that forms a monolayer on the membrane surface, leading to the onset of membrane fouling and pore wetting [36]. Adsorption of these unimers onto hydrophobic membrane surfaces is predominantly through hydrophobic (non-polar tails) interactions. The hydrophobic-hydrophobic interaction is governed by the hydrophobicity of a surfactant unimer, which is determined by its HLB value [37]. The smaller the HLB value, the more hydrophobic the surfactant is, which in turn suggests a greater affinity for hydrophobic surfaces [22]. In contrast, surfactants with lower hydrophobicities have an affinity for the aqueous feed. When surfactant concentration in the feed stream exceeds the CMC value, surfactant unimers are likely to pack more densely on hydrophobic membrane

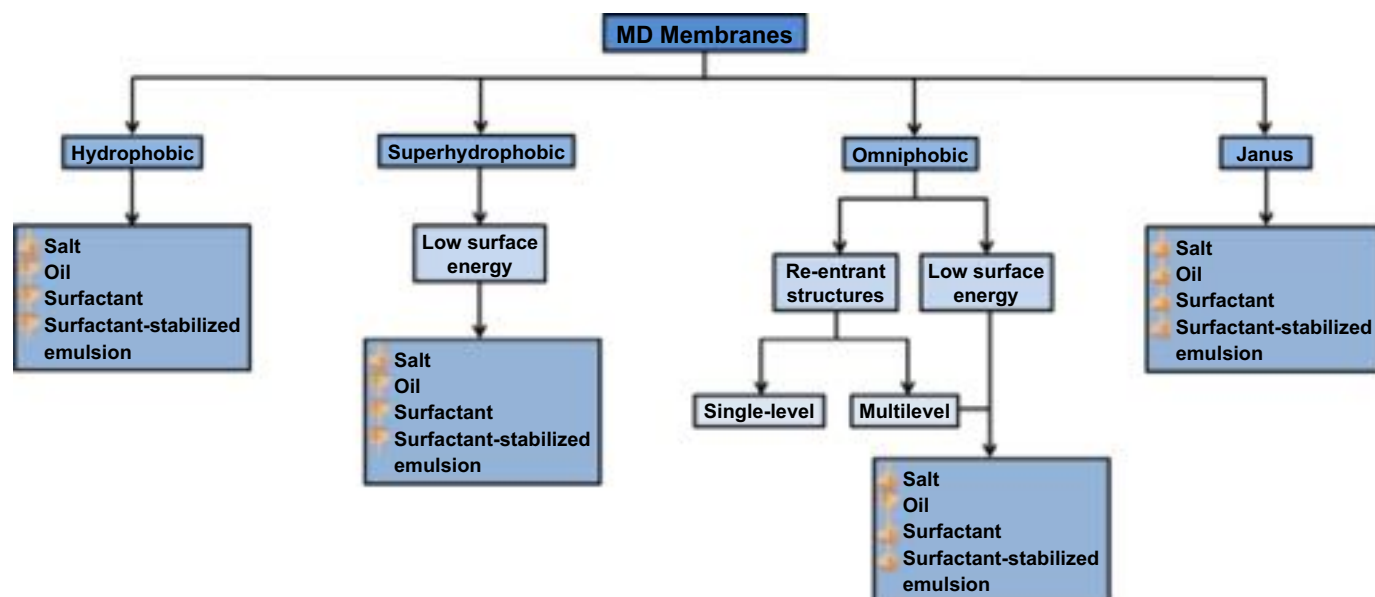


Fig. 2. Different types of MD membrane.

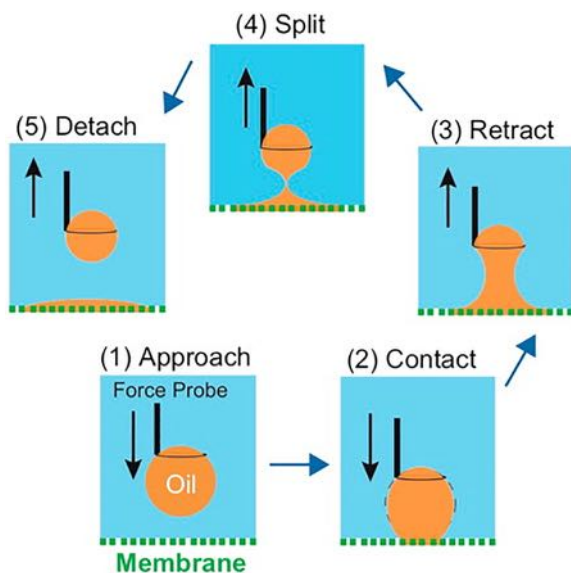


Fig. 3. Five distinct events are involved in the interaction between the mineral oil droplet and the hydrophobic membrane surface. Images are reproduced with permission from the American Chemical Society [38].

surfaces, leading to severe fouling [22]. In addition, once anchored on the membrane surface, surfactants with larger hydrophilic head-groups have higher tendencies of drawing the aqueous feed towards the membrane pores, giving on to pore wetting [22].

The underwater force adhesion measurement between a hydrophobic porous membrane surface and a tethered oil droplet allows us to mechanistically elucidate the fouling propensity of conventional MD membranes in oil-containing feed streams. This process is governed by five distinct events as illustrated in Fig. 3 [38]. The adhesion force for Event (1) is zero by default. A significant and abrupt increase in the adhesion is observed in Event (2) due to the strong hydrophobic-hydrophobic interaction between the oil droplet and the membrane surface. There is a gradual increase in adhesion force during Event (3) as the oil droplet continues to be stretched. When the oil droplet is eventually split from the membrane surface in Event (4), a precipitous drop in adhesion force can be detected. An artifact of 'positive' adhesion force is recorded for Event (5). This can be attributed to the floating

force on a smaller remaining oil droplet being lower than the original larger oil droplet tethered from the force probe.

Wang et al. compared the performances of hydrophobic, omniphobic, and composite (otherwise known as Janus) MD membranes in different surfactant- and oil-containing feed solutions as shown in Fig. 4 [39]. The definitions of omniphobic and Janus membranes will be provided in detail in the next section. In Fig. 4, it illustrates that conventional hydrophobic MD membranes are prone to fouling and wetting in every low-surface-tension solution. In contrast, omniphobic MD membranes are wetting-resistant to O/W emulsions with excess surfactants, but are prone to fouling during treatment of O/W emulsions without surfactants. Janus MD membranes are generally oil-fouling-resistant, but may experience wetting in the presence of excess surfactants. Both omniphobic and Janus MD membranes have their respective strengths and limitations. Thus, the concept of leveraging and combining the desirable attributes of both membranes for the development of bespoke MD membranes is certainly interesting, and will be discussed in the subsequent sections of this review. Nonetheless, this particular study by Wang et al. provides us with a guide to the development of different membranes tailored for various surfactant- and oil-containing feed streams but should not be taken at face value since a combination of factors (surface charge, surface energy, surface structures, surface chemistry, and etc.) usually determines the actual performances of these membranes in real applications. The following sections will include detailed discussions on what omniphobic and Janus MD membranes are, and how the development of these membranes has evolved throughout the years (as listed in Table 1).

3. Different types of MD membrane for surfactant- and oil-containing feed streams

3.1. Wenzel state and Cassie-Baxter state

Unlike ideal surfaces, membrane surfaces often possess rough textures and/or chemical heterogeneity. This typically results in either of the two wetting regimes: homogenous or heterogeneous. Both regimes are disparate in nature, and have varied effects on the contact angles of wetting liquids on membrane surfaces. As illustrated in Fig. 5, the Wenzel and Cassie-Baxter models have been developed to describe these wetting phenomena on textured surfaces

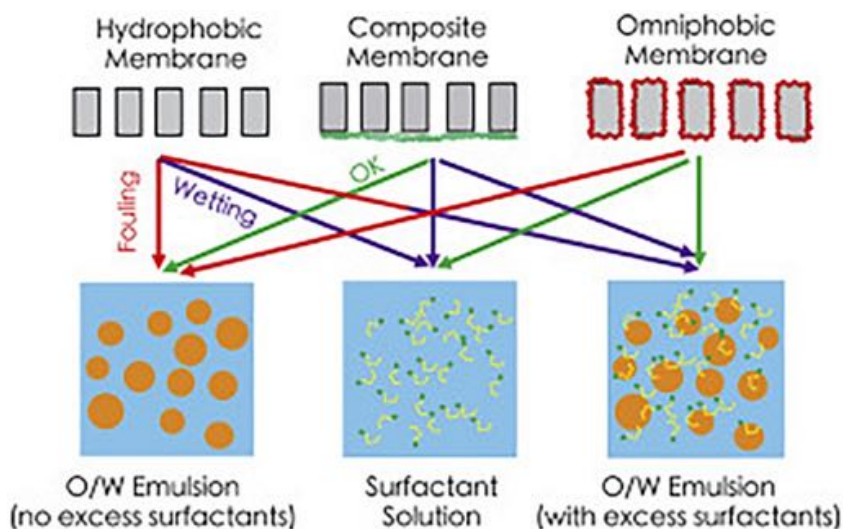


Fig. 4. Fouling- and wetting-resistant properties of different membranes in low-surface-tension feed solutions. Images are reproduced with permission from Elsevier [39]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Table 1

An overview of recent advances in membrane development for surfactant- and oil-containing feed streams in terms of fabrication approaches, performances, and enhancements.

Membrane type	Major materials	Fabrication method	MD configuration	Operating conditions	Type of feed	Membrane performance	Value-added characteristics	Ref
Omniphobic flat-sheet	PVDF-HFP/FAS17/SiNP/APTES/glass fiber	Dip-coating	DCMD	T _f : 333 K T _p : 293 K	Up to 0.4 mM SDS	No fouling and wetting for 9 h	LCA ≈ 80° in ethanol	[46]
Omniphobic flat-sheet	PFTS/SiNP/PVDF	Dip-coating	DCMD	T _f : 349 K T _p : 293 K	10 mg L ⁻¹ kerosene, 10 mg L ⁻¹ humic acid, and 10 mg L ⁻¹ SDBS	No fouling and wetting for up to 120 h	N.A.	[47]
Omniphobic flat-sheet	FAS17/SiNP/APTES/glass fiber	Dip-coating	DCMD	T _f : 333 K T _p : 293 K	Up to 0.3 mM SDS	No fouling and wetting for 8 h	LCA ≈ 100° in ethanol	[48]
Omniphobic flat-sheet	FDTS/SiNP/APTES/PVDF	Dip-coating	DCMD	T _f : 333 K T _p : 293 K	Up to 0.2 mM SDS	No fouling and wetting for 8 h	Robust under chemical and physical stresses	[49]
Omniphobic hollow fiber	Teflon AF 2400/SiNP/APTES/PVDF	NIPS and dip-coating	VMD	T _f : 343 K	Up to 0.6 mM SDS	No wetting for 7 h	LCA ≈ 70° in ethanol	[50]
Omniphobic flat-sheet	SiNP/APTES/PVDF	Dip-coating	DCMD	T _f : 333 K T _p : 293 K	Surfactant-stabilized O/W emulsion	No fouling and wetting for 16 h	LCA ≈ 138° in hexadecane	[51]
Omniphobic flat-sheet	PVDF-HFP/FAS/ZnO/glass fiber	CBD and dip-coating	DCMD	T _f : 333 K T _p : 293 K	Up to 0.3 mM SDS	No fouling and wetting for 8 h	LCA ≈ 110° in ethanol	[52]
Omniphobic hollow fiber	FAS17/ZnO/alumina	Combined phase inversion and sintering, CBD, and dip-coating	DCMD	T _f : 343 K T _p : 288 K	Up to 2 mM SDS	No fouling and wetting for 24 h	LCA ≈ 138° in 90% v/v ethanol/water mixture	[53]
Omniphobic flat-sheet	FAS/ZnO/PVDF-HFP/PVDF	Electrospraying	DCMD	T _f : 333 K T _p : 293 K	Up to 0.4 mM SDS and 0.015% v/v O/W emulsion	Some wetting and fouling in high concentration solutions	LCA ≈ 130° in ethanol	[54]
Omniphobic flat-sheet	PDAA/FAS17/SiA/PVDF	NIPS and LBL	AGMD	T _f : 333 K T _p : 293 K	Up to 0.5 mM SDS	No fouling and wetting for 12 h	LCA ≈ 160° in methanol and enhanced mechanical and thermal properties	[56]
Omniphobic nanofiber	FDTS/SiNP/PVDF-HFP/BTEAC	Electrospinning and dip-coating	DCMD	T _f : 333 K T _p : 293 K	Up to 0.3 mM SDS	No fouling and wetting for 8 h	LCA ≈ 110° in ethanol	[57]
Omniphobic nanofiber	FTCS/PVDF	Electrospinning and dip-coating	DCMD	T _f : 333 K T _p : 293 K	Up to 0.1 mM SDS	No fouling and wetting for 6 h	Robust under ultrasonication	[58]
Omniphobic nanofiber	FAS17/PVDF-HFP	Electrospinning and dip-coating	DCMD	T _f : 338 K T _p : 298 K	Up to 0.1 mM SDS	No fouling and wetting for 2 h	Robust under chemical and thermal stresses	[59]
Omniphobic nanofiber	CF ₄ /PVDF	Electrospinning and plasma treatment	AGMD	T _f : 333 K T _p : 293 K	Up to 0.7 mM SDS	No fouling and wetting for 10 h	LCA ≈ 100° in methanol	[60]
Omniphobic nanofiber	SiNP/PVA	Electrospinning	DCMD	T _f : 333 K T _p : 293 K	Up to 0.4 mM SDS	No fouling and wetting for 5 h	LEP ≈ 91 kPa	[61]
Omniphobic nanofiber	F-POSS/PVDF-HFP	Electrospinning	DCMD	T _f : 333 K T _p : 293 K	Up to 0.3 mM SDS	No fouling and wetting for 8 h	LCA ≈ 130° in ethanol	[62]
Janus flat-sheet	SiNP/APTES/PVDF-HFP/FAS17/SBMA/quartz fiber	Dip-coating and surface-initiated ATRP	DCMD	T _f : 333 K T _p : 293 K	Up to 0.2 mM SDS and 530 mg L ⁻¹ surfactant-stabilized O/W emulsion	No fouling and wetting for 12 h	N.A.	[12]
Janus hollow fiber	PDA/PEI/PVDF	Dip-coating	DCMD	T _f : 333 K T _p : 293 K	50 mg L ⁻¹ Tween® 20, 50 mg L ⁻¹ DTAB, and 500 mg L ⁻¹ surfactant-stabilized O/W emulsion	No fouling and wetting for up to 168 h	Robust under ultrasonication	[23]
Janus hollow fiber	PDA/sodium periodate/PVDF	Dip-coating	DCMD	T _f : 333 K T _p : 293 K	50 mg L ⁻¹ Tween® 20, 50 mg L ⁻¹ SDS, 50 mg L ⁻¹ DTAB, and 500 mg L ⁻¹ surfactant-stabilized O/W emulsion	No fouling and wetting for up to 140 h	Robust under ultrasonication and flux enhancement of up to 70% in 3.5 wt % NaCl at 333 K	[24]
Janus hollow fiber	PDA/sodium periodate/AgNP/PVDF	Dip-coating	DCMD	T _f : 333 K T _p : 293 K	50 mg L ⁻¹ Tween® 20 and 500 mg L ⁻¹ surfactant-stabilized O/W emulsion	No fouling and wetting for up to 96 h	Robust under ultrasonication and flux enhancement of up to 58% in 3.5 wt % NaCl at 333 K	[25]

(continued on next page)

Table 1 (continued)

Membrane type	Major materials	Fabrication method	MD configuration	Operating conditions	Type of feed	Membrane performance	Value-added characteristics	Ref
Janus flat-sheet	CTS/PFO/SiNP/PVDF	Dip-coating	DCMD	T _f : 333 K T _p : 293 K	1000 ppm O/W emulsion	No fouling and wetting for 36 h	LCA ≈ 150° in oil underwater	[38]
Janus flat-sheet	PEG/TiO ₂ /PVDF	Dip-coating and plasma treatment	DCMD	T _f : 333 K T _p : 293 K	0.01 wt% O/W emulsion	No fouling and wetting for 24 h	N.A.	[69]
Janus flat-sheet	agarose/PTFE	Dip-coating	DCMD	T _f : 333 K T _p : 294 K	10 mg L ⁻¹ Tween® 20 and 500 mg L ⁻¹ SDS	No fouling and wetting for 24 h	N.A.	[70]
Janus flat-sheet	PDDA/PAA/PVDF	Dip-coating	DCMD	T _f : 341 K T _p : 295 K	10 mg L ⁻¹ Tween® 80, 30 mg L ⁻¹ CTAB, and 50 mg L ⁻¹ SDS	No fouling and wetting for up to 8 h in CTAB and SDS solutions	N.A.	[71]
Janus flat-sheet	PDA/SiNP/PVDF	Dip-coating	DCMD	T _f : 333 K T _p : 293 K	1000 ppm O/W emulsion	No fouling and wetting for 12 h	LCA ≈ 158° in oil underwater	[72]
Janus flat-sheet	SBMA/PVDF	Dip-coating and plasma treatment	DCMD	T _f : 338 K; 318 K T _p : 288 K	Numerous	Varied	N.A.	[73]
Janus flat-sheet	FS/CTS/PFO/PVDF	Dip-coating and spray-coating	DCMD	T _f : 333 K T _p : 293 K	1000 ppm O/W emulsion	No fouling and wetting for 36 h	LCA ≈ 139° in oil in air	[74]
Janus flat-sheet	PDA/PTFE	Dip-coating	VMD	T _f : 333 K	500 mg L ⁻¹ mineral oil	No wetting for up to 40 h	Threefold flux enhancement in 3.5 wt% NaCl at 343 K	[76]
Janus nanofiber	CTS/PFO/SiNP/CTAB/ PVDF-HFP	Electrospinning, dip-coating, and chemical vapor deposition	DCMD	T _f : 333 K T _p : 293 K	1000 ppm O/W emulsion and up to 0.4 mM SDS	No fouling and wetting for 10 h	LCA ≈ 140° in oil underwater	[77]
Janus flat-sheet	CA/SiNP/PTFE	Electrospinning	DCMD	T _f : 326 K T _p : 293 K	1000 mg L ⁻¹ O/W emulsion	No fouling and wetting for 30 h	Comparable flux to pristine membrane	[78]
Janus flat-sheet	EDA/PEI/PVDF	Electrospinning and dip-coating	DCMD	T _f : 328 K T _p : 293 K	1000 mg L ⁻¹ crude oil	No fouling and wetting for 60 h	N.A.	[79]
Janus flat-sheet	GA/PVA/PTFE	Electrospinning and dip-coating	DCMD	T _f : 326 K T _p : 293 K	1000 mg L ⁻¹ O/W emulsion	No fouling and wetting for 30 h	LCA ≈ 150° in oil underwater	[80]
Janus flat-sheet	Polyurethane/PTFE	N.A.	DCMD	T _f : 333 K T _p : 283 K	40 mg L ⁻¹ SDS	No fouling and wetting	N.A.	[81]
Janus nanofiber	FAS/SiNP/PAN/PS/PVDF-HFP	Electrospinning and electrospaying	DCMD	T _f : 333 K T _p : 293 K	1000 ppm O/W emulsion	No fouling and wetting for 30 h	Comparable flux to pristine membrane	[82]
Janus flat-sheet	GO/PVDF	Dip-coating	DCMD	T _f : 338 K T _p : 293 K	50 mg L ⁻¹ SDBS	No fouling and wetting for 5 h	Comparable flux to pristine membrane	[83]

[40]. The Wenzel model describes the homogenous wetting regime on rough surfaces with chemical homogeneity [41]. In this regime, the liquid fully penetrates into the asperities on the membrane surface such that it maximizes the liquid-solid interface. The Wenzel model is governed by the following equation:

$$\cos\theta^* = r \cos\theta \quad (1)$$

where θ^* is the apparent contact angle, r is the roughness ratio of the actual area to the projected area of the membrane surface ($r = 1$ for a smooth surface and > 1 for a rough one), and θ is the equilibrium contact angle of an ideal surface. Eq. (1) states that the presence of rough structures will further enhance the wettability of surfaces (both hydrophilic and hydrophobic) in the Wenzel state. In other words, a hydrophilic surface becomes more hydrophilic whereas a hydrophobic surface becomes more hydrophobic.

In contrast, the heterogeneous wetting regime on chemically heterogeneous surfaces is more complex as it involves the formation of a composite surface that has regions of both air and solid. Hence, the Wenzel equation cannot sufficiently explain the wetting regime.

Instead, the Cassie-Baxter equation is often applied for these surfaces [42]:

$$\cos\theta^* = f_1 \cos\theta - f_2 \quad (2)$$

where θ^* is the apparent contact angle, θ is the equilibrium contact angle of an ideal surface, and f_1 and f_2 are area fractions of the solid-liquid and liquid-air interfaces, respectively. In the Cassie-Baxter state, the contact angle increases with the area fraction of the liquid-air interface. This is possible through the creation of omniphobic membrane surfaces.

3.2. Engineering omniphobic membranes with multilevel re-entrant structures

In low-surface-tension liquids, the Cassie-Baxter state is a thermodynamically-unstable state [17]. Owing to this fact, achieving wetting-resistant property against these liquids is no easy task. In 2008, scientists from the Massachusetts Institute of Technology invented omniphobic surfaces, which literally means that these special surfaces when exposed to air could not be wetted by any liquid [43].

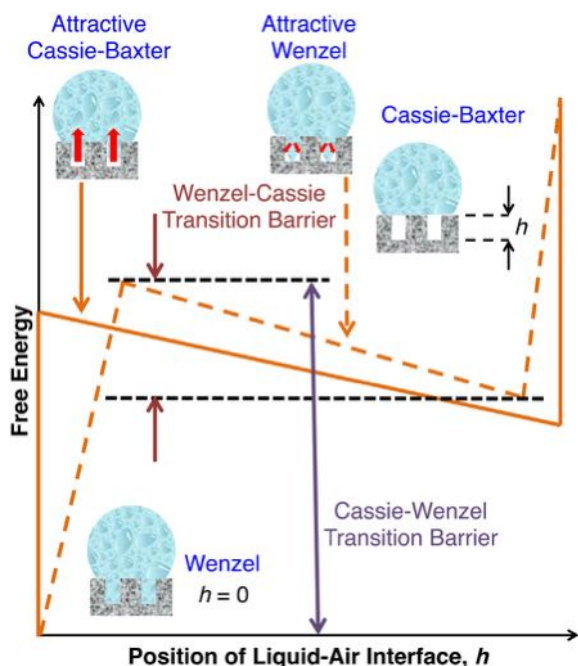


Fig. 5. Free energy as a function of the position of liquid-air interface [40].

Since then, omniphobic membranes have gained increased attention in the field of MD due to their interesting surface properties. Omniphobic surfaces are similar to superhydrophobic surfaces in the sense that they require minimal surface-energy, but there the similarity ends. An ideal omniphobic surface should have overhanging geometry features that endow it with both in-air non-wetting (high apparent contact angle) and easy droplet roll-off (low contact angle hysteresis) properties [43]. Without the presence of re-entrant structures, wicking of substrate pores in low-surface-tension fluids becomes thermodynamically favorable (as in the case of superhydrophobic surfaces). Only through coupling minimal surface-energy and re-entrant structures, it is possible to achieve the thermodynamically-metastable Cassie-Baxter state that represents a significant local kinetic barrier to slow down its transition to the fully-wetted Wenzel state. Theoretically, this makes it feasible for omniphobic surfaces to repel liquids regardless of their surface-tensions, and thus exhibit low wettabilities by water, surfactants, and oils [44].

As depicted in Fig. 6, the main characteristic of a re-entrant structure is that the air voids between the liquid and solid interfaces widen as the low-surface-tension liquid descends towards the structure. As the liquid penetrates into such a structure, the surface area of the liquid-air interface grows larger. The thermodynamically-metastable Cassie-Baxter state represents a kind of temporary energy trap. As such, to transition from this state to the fully-wetted Wenzel state, a significant amount of energy/pressure is required to overcome this barrier [17]. However, this metastable state represents only the local free-energy minimum (Cassie-Baxter) and not the global free-energy minimum (Wenzel). Furthermore, re-entrant geometries need to be designed in such a way that the equilibrium contact angle, θ , is always greater than or equal to the surface's local geometric angle, ψ . This will allow the liquid-air interface to recede to the top of the re-entrant structures, maintaining a composite solid-liquid-air interface during operations [43]. While the design of such surfaces can be rather challenging, it is evident that the presence of re-entrant structures holds potential for the treatment of surfactant- and oil-containing wastewaters via the MD process.

Omniphobic membrane surfaces are typically engineered with single-level or multilevel re-entrant structures as illustrated in Fig. 7. Multilevel re-entrant structures are generally preferred for surfactant- and oil-containing feed streams in MD applications as these structures can achieve superomniphobicity and serve as an additional barrier to pore wetting [45]. To construct re-entrant structures, several techniques have been proposed: (i) dip-coating; (ii) chemical bath deposition (CBD); (iii) layer-by-layer (LBL) assembly; (iv) plasma treatment; and (v) electrospinning. In the dip-coating technique, commercially available membranes with hierarchical surface structures such as glass fiber membranes are generally selected as substrate materials since their cylindrical surface morphologies can provide primary re-entrant structures. In addition, the abundant hydroxyl-functional groups present on these substrate surfaces are ideal for surface-modification. As pioneers, Lin et al. improvised this concept to fabricate microporous omniphobic membranes with multilevel re-entrant structures for MD applications [46]. Silica nanoparticles (SiNP) (secondary re-entrant structures) were coated onto hydrophilic glass fiber membranes (primary re-entrant structures) followed by surface fluorination (ultralow surface energy) and polymer coating (to achieve thermodynamically-metastable Cassie-Baxter state). No wetting was observed for 9 h of test duration in the presence of an anionic surfactant, sodium dodecyl sulfate (SDS). This result demonstrated the potential of applying omniphobic membranes for the desalination of surfactant-containing feed water via the MD process. The membranes' wetting-resistant

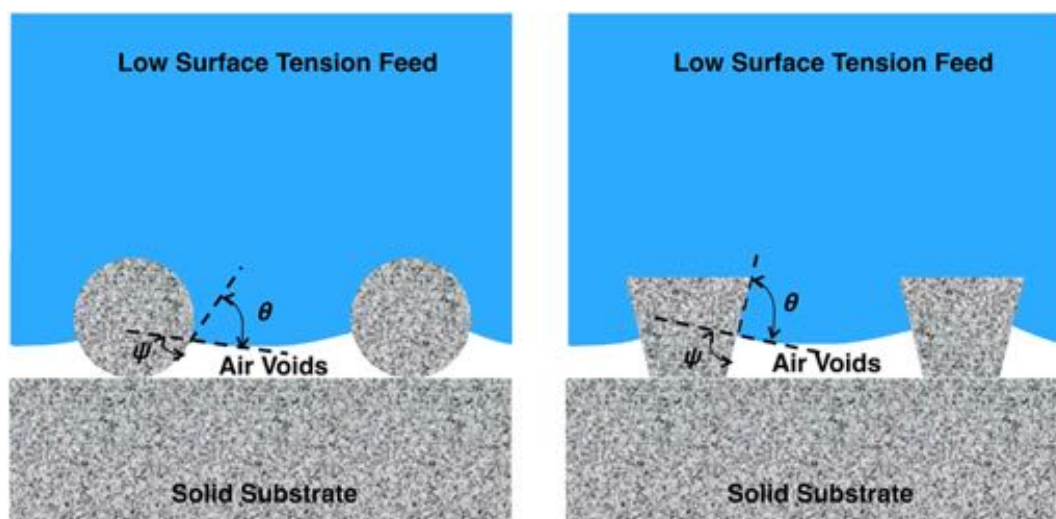


Fig. 6. Schematic of two different textured surfaces with potential barriers for Cassie-Wenzel transition.

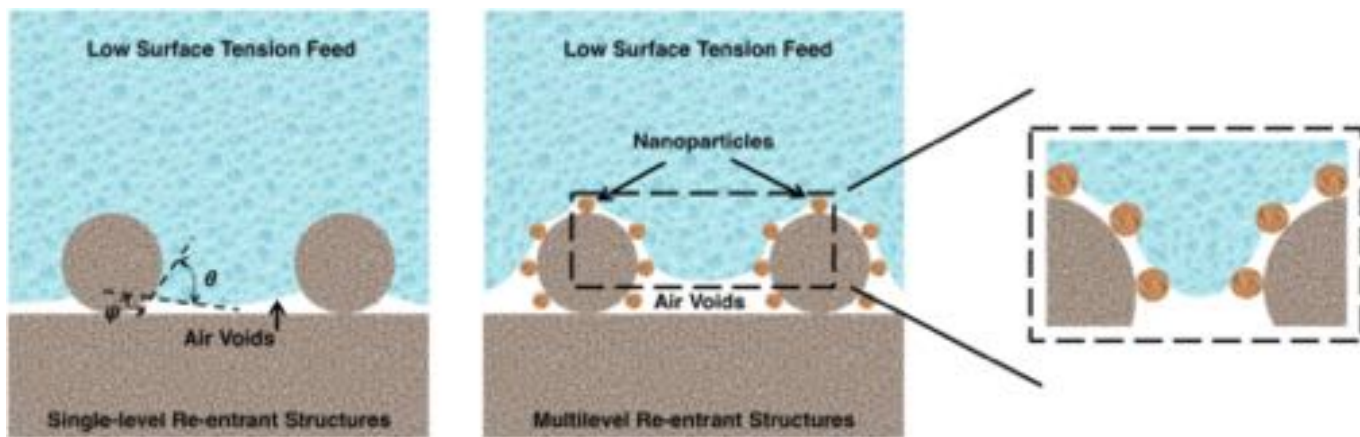


Fig. 7. Schematic of single-level and multilevel re-entrant structures.

properties were attributed to the creation of multilevel re-entrant structures. This coupled with their newly-acquired ultralow-surface-energy allowed for the existence of a thermodynamically-metastable Cassie-Baxter state for composite solid-liquid-air interfaces. Based on this principle, the development of omniphobic membranes for MD applications has picked up the pace in recent years [47].

In another study deploying the dip-coating technique, Boo and co-workers conducted comparison tests between single-level and multilevel re-entrant structures with different surface-energies [48]. While the deposition of SiNP creates re-entrant structures, it was revealed in this study that the introduction of ultralow-surface-energy materials to the membrane surface does not alter or have an undesirable effect on membrane surface morphology. Their study also provided further validation that the creation of multilevel re-entrant structures with ultralow-surface-energies is the key to surface superomniphobicity,

which in turn is a major contributing factor to engineering fouling- and wetting-resistant surfaces for low-surface-tension solutions. It was elucidated that while re-entrant structures could resist wetting by oil droplets, ultralow-surface-energies could endow membranes with fouling-resistant properties against oil droplets. This finding was supported by a similar study [49].

Previous studies have validated the potential of utilizing SiNP in engineering multilevel re-entrant structures but neglected the effects of SiNP size on membrane surface properties and accompanying performances. In a recent study, Lu et al. investigated the effects of SiNP size on membrane omniphobicity (Fig. 8) [50]. The results suggest that smaller-sized nanoparticles exhibit better repellency against low-surface-tension liquids ascribing to the negligent gap-space between neighboring nanoparticles that prevents transition from the thermodynamically-metastable Cassie-Baxter phase to the

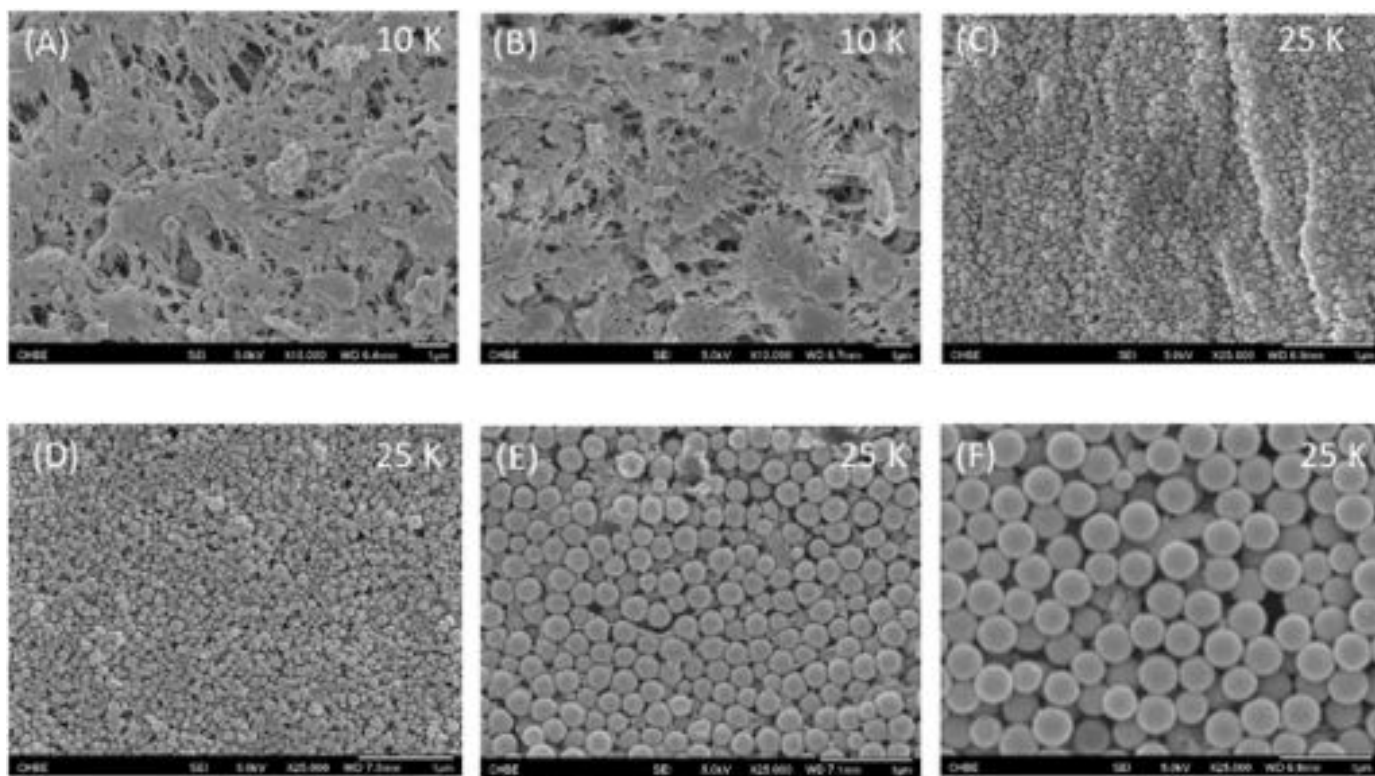


Fig. 8. Field emission scanning electron microscopy (FESEM) images of the outer membrane surfaces of (a) neat PVDF membrane, (b) PVDF membrane with Teflon coating, (c) PVDF membrane coated with 60 nm nanoparticles, (d) PVDF membrane coated with 60 nm nanoparticles and Teflon, (e) PVDF membrane coated with 250 nm nanoparticles and Teflon, and (f) PVDF membrane coated with 400 nm nanoparticles and Teflon. Images are reproduced with permission from the American Chemical Society [50].

fully-wetted Wenzel phase. However, smaller-sized nanoparticles tend to be deposited into larger membrane pores and block vapor flow channels, thus leading to slightly lower flux. Besides that, Lu and coworkers introduced a more convenient and facile way of lowering the surface-energies of membranes by utilizing Teflon AF 2400. In a separate study shown in Fig. 9, Zheng et al. created hierarchical microspheres via electrostatic adsorption between negatively-charged SiNP and positively-charged polystyrene, and deposited these microspheres onto functionalized commercial PVDF membranes using a bonding agent to create multilevel re-entrant structures [51]. By using a bonding agent, the robustness of the membranes was enhanced. The membranes delivered excellent performance in a surfactant-stabilized O/W emulsion for up to 1000 min of continuous operation. It was further confirmed that lowering the surface-energies of membrane surfaces alone is not enough to circumvent the occurrence of membrane fouling and pore wetting in surfactant- and oil-containing feed waters. Furthermore, depositing nanoparticles that are smaller than the membrane pores will lead to pore blockages, which in turn result in low flux. These results were in good agreement with Lu et al.'s findings [50]. This study validated that by coupling the effects of multilevel re-entrant structures and low surface energies, omniphobic MD membranes could achieve fouling- and wetting-resistant properties in surfactant- and oil-containing waste streams. The dip-coating technique is simple and straightforward but requires better utilization of the coating solutions and simplification of the preparation steps in order to be included as a viable option for large-scale fabrication.

Chen et al. introduced the CBD technique for surface-engineering by depositing zinc oxide (ZnO) nanoparticles onto hydrophilic glass fiber membranes [52]. An advantage of using ZnO nanoparticles as an alternative material to create re-entrant structures is that they can be synthesized via low-cost and scalable techniques with readily available raw materials. Polymer coating was subsequently carried out to immobilize the ZnO nanoparticles and enhance their durability as shown in Fig. 10. The omniphobic membranes were able to sustain a stable flux with excellent rejection in SDS solution during 8 h of test duration. An advantage of CBD is that it yields a reproducible and uniform layer of

multilevel re-entrant structures with good stability. A downside of CBD is the wastage of chemical solutions after each round of deposition. In a separate but similar work, Chen et al. deposited ZnO nanorods and nanoparticles on alumina hollow fiber membranes via the CBD technique [53]. The presence of ZnO nanostructures enhanced the surface roughness of the alumina substrates, and the surface-modified membranes exhibited excellent wetting-resistant properties in low-surface-tension feed solutions. In a word, these studies have shown the versatility of the CBD technique in the sense that it could be applied to both flat-sheet and hollow fiber membranes of different materials. A recent work by Deka et al. explored the method of electrospraying ZnO nanoparticles to obtain uniform hierarchical re-entrant structures formed by microspheres and demonstrated similar performances in low-surface-tension feed streams [54].

The LBL technique is often regarded to as one of the most straightforward methods to engineer hierarchical structures on membrane surfaces. It is also a relatively inexpensive technique with a huge potential for large-scale fabrication due to the fact that it generally involves the use of environmentally friendly chemicals [55]. As shown in Fig. 11, Woo and coworkers improvised this technique to create omniphobic MD membranes with improved mechanical and thermal properties via electrostatic interaction between negatively-charged silica aerogel (SiA) and positively-charged poly(diallyldimethylammonium chloride) (PDDA) [56]. Re-entrant surface structures were created through the deposition of SiA whereas the formation of trifluoromethyl and tetrafluoroethylene bonds rendered the substrate surfaces with minimal surface-energy. A major disadvantage of the LBL technique is that it usually involves numerous surface modification steps and creates dense active layers on membrane substrates, leading to decreased permeation flux. Thus, a balance between the number of deposited layers and membrane performances needs to be struck in any future work that deploys the LBL technique.

Electrospinning offers a practical option for the fabrication of omniphobic MD membranes due to its versatility and ease of operation [43]. A major advantage of this technique is that it allows the use of different base polymers and imparts them with tunable pore sizes

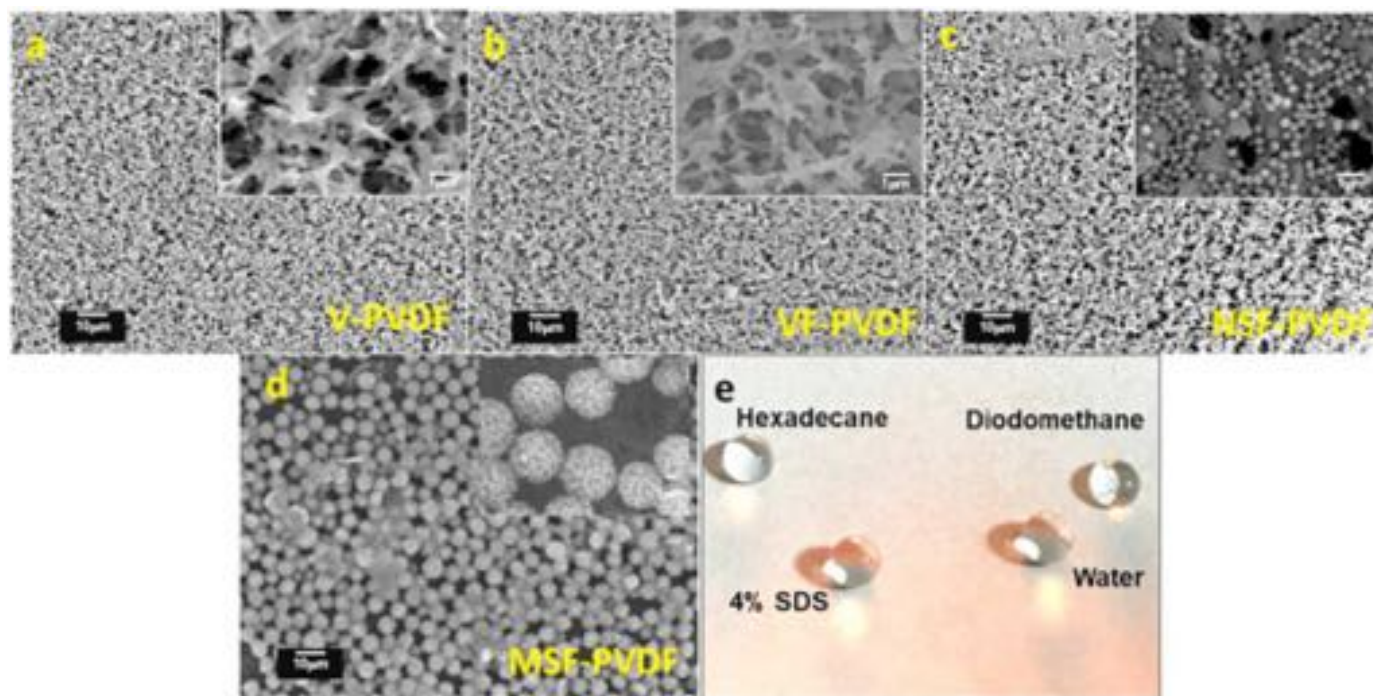


Fig. 9. Scanning electron microscopy (SEM) images of (a) commercial PVDF membrane (V-PVDF), (b) fluorinated PVDF membrane (VF-PVDF), (c) fluorinated PVDF membrane coated with 450 nm SiNP (NSF-PVDF), and (d) fluorinated PVDF membrane coated with hierarchical microspheres (MSF-PVDF). (e) A photograph of various droplets on the MSF-PVDF surface. Images are reproduced with permission from Elsevier [51].

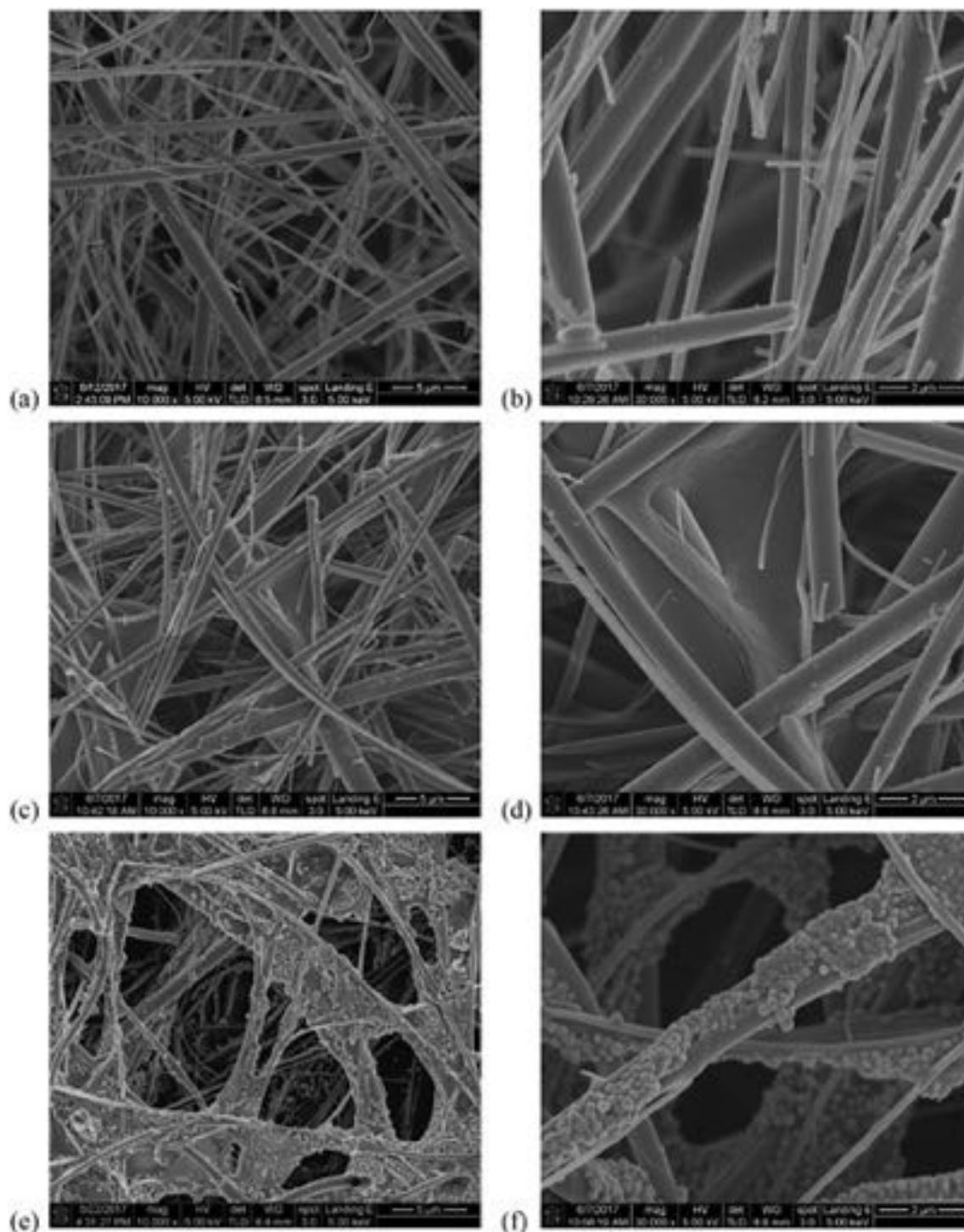


Fig. 10. SEM images of different magnifications of (a, b) glass fiber membrane modified by FAS17, (c, d) glass fiber membrane modified by FAS17 and polymer coating, and (e, f) glass fiber membrane with ZnO nanoparticles modified by FAS17 and polymer coating. Images are reproduced with permission from Elsevier [52].

amongst other desirable properties. Electrospun nanofibers possess cylindrical geometries that offer primary re-entrant structures, and could be further manipulated for the construction of secondary levels of re-entrant structures. Lee and co-workers laid the groundwork for fabrication of mechanically- and chemically-robust omniphobic MD membranes by combining the electrospinning and dip-coating techniques [57]. Cylindrical electrospun nanofibers were used as scaffolds for subsequent surface-modification with spherical SiNP and ultralow-surface-energy materials. Their newly developed omniphobic membranes exhibited wetting-resistant properties against liquids with surface-

tensions as low as 22.1 mN m^{-1} , and demonstrated stable performance in an 8 h operation where SDS-containing solution was used as feed. While previous studies delved into the use of nanoparticles to create rough hierarchical structures, Deng et al. endowed PVDF electrospun nanofibrous membranes with omniphobic properties by introducing self-roughening fluorododecyltrichlorosilane (FTCS) [58]. By increasing the concentration of FTCS, the morphologies of the nanofibers evolved from newly-budding willow twigs with tiny bumps to intertwined fillets as shown in Fig. 12. Highly cross-linked Si-O-Si networks present on the omniphobic membrane surfaces enhanced their mechanical

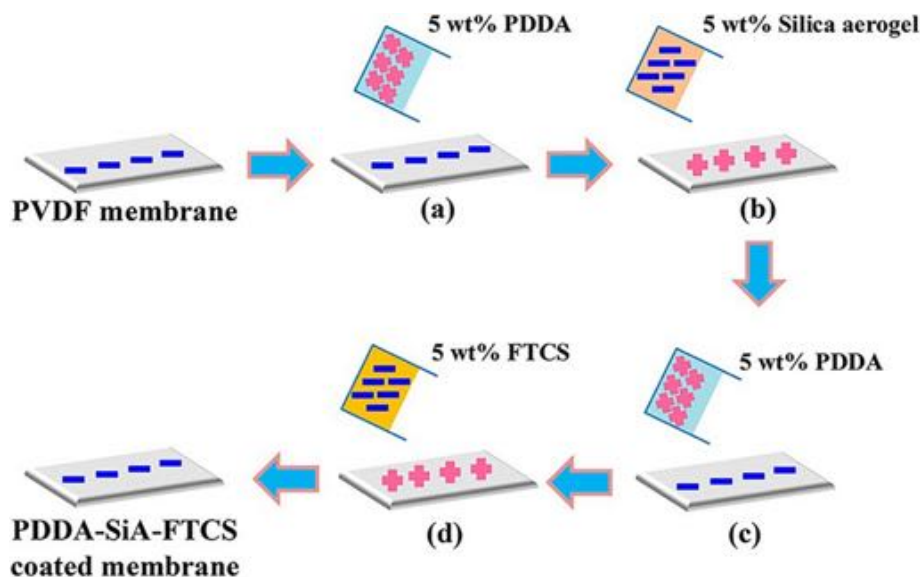


Fig. 11. Schematic diagram illustrating application of the LBL technique for engineering of omniphobic MD membranes. Images are reproduced with permission from the American Chemical Society [56].

properties. Besides that, the membranes remained robust and minimal changes to their surface properties and surface morphologies were observed after 20 min of ultrasonication. This novel technique produced membranes with competitive flux while maintaining an excellent salt rejection property in a surfactant-containing feed solution during 6 h of operation. In another study, An et al. dip-coated nanofibers with fluorinated solutions to fabricate omniphobic MD membranes that remained robust after being subjected to a series of harsh conditions such as boiling in water as well as strong acid and base etching treatments [59].

Plasma treatment is another interesting surface-modification technique that is highly-scalable and able to produce robust coatings. Woo et al. employed tetrafluoromethane (CF_4) plasma modification on electrospun PVDF nanofibers to achieve omniphobicity [60]. It was revealed that plasma treatment of merely 15 min could impart the lotus effect on the modified membrane surfaces and increase their LEP significantly.

Most of the studies on omniphobic MD membranes reported thus far have involved numerous preparation steps. For practical implementation, hassle-free single-step techniques need to be developed. While prior studies have combined the electrospinning technique with other surface-modification techniques, Huang et al. broke new grounds by turning to single-step coaxial electrospinning for the preparation of omniphobic membranes [61]. This allows for better utilization of SiNP. The omniphobic membranes consisted of two levels of re-entrant structures. The fibrous network provided the primary level of re-entrant texture whereas SiNP present on the nanofibers formed the secondary level of re-entrant structures. This novel technique provides an alternative to the dip-coating technique for the formation of multilevel re-entrant structures and controlled deposition of SiNP for sustainable operations in surfactant-containing wastewaters. In another study, Lu et al. demonstrated one-step in-situ formation of omniphobic MD membranes via electrospinning of fluorinated-decyl polyhedraloligomeric silsesquioxane (F-POSS) based nanofibers without the use of fluorinated solvents [62]. From the SEM images presented in Fig. 13, minimal changes to membrane surface morphologies were observed with the addition of F-POSS. The near-perfect formation of nanofibers with unitary microstructures suggests that good dispersion of F-POSS in the dope solution was achieved, which was ascribed to the excellent intermolecular forces between the fluoroalkyl groups on the periphery of F-POSS and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). These novel

omniphobic MD membranes demonstrated fouling- and wetting-resistant properties in SDS solution throughout 8 h of test duration.

As reviewed thus far, omniphobic MD membranes indeed have the potential to be applied for surfactant- and oil-containing feed streams. While the results for these membranes look promising, it is worth noting that many of the reviewed studies only focused on the rejection of an anionic surfactant, SDS. Since real water samples often contain a wide range of surfactants and oils, these observations would have been of more value had these membranes been tested in more complex feed solutions. Moreover, there remain numerous challenges in the scalable fabrication of operationally-stable omniphobic MD membranes for practical applications. These challenges include the engineering of faultless and tedious surface morphologies as well as the complexity involved in these emerging fabrication processes that drives up the production cost [33]. Another potential pitfall of omniphobic MD membranes is the use of highly-fluorinated solvents in fabrication processes that are carcinogenic. More environmentally friendly fabrication procedures need to be developed for wider acceptance of omniphobic MD membranes in practical applications. In addition, more rigorous and long-term assessment tests need to be conducted in tandem when nanoparticles are involved in the fabrication of omniphobic MD membranes to ensure that these nanoparticles do not leach into the distillate stream.

3.3. Engineering Janus membranes

A Janus membrane is a membrane with asymmetric properties on either side of the membrane or at membrane interfaces [63]. Conventionally, one side/interface of the membrane is lyophilic whereas its other side/interface is lyophobic. Janus membranes were first proposed for the MD process due to the need for membranes with higher flux for desalination purposes [64]. This could be achieved by creating a hydrophilic layer on the side of the membrane facing the permeate stream, leading to faster vapor removal due to reduced mass transfer resistance and lower conductive heat loss [65–68]. Recently, a plethora of Janus MD membranes have reemerged for application in surfactant- and oil-containing feed waters. Four different configurations of Janus MD membranes have been established for these applications: (i) superhydrophilic-hydrophobic; (ii) superhydrophilic-omniphobic; (iii) superhydrophilic-hydrophobic-hydrophilic; and (iv) superhydrophilic-superhydrophobic-hydrophobic. For conventional configurations such as superhydrophilic-hydrophobic

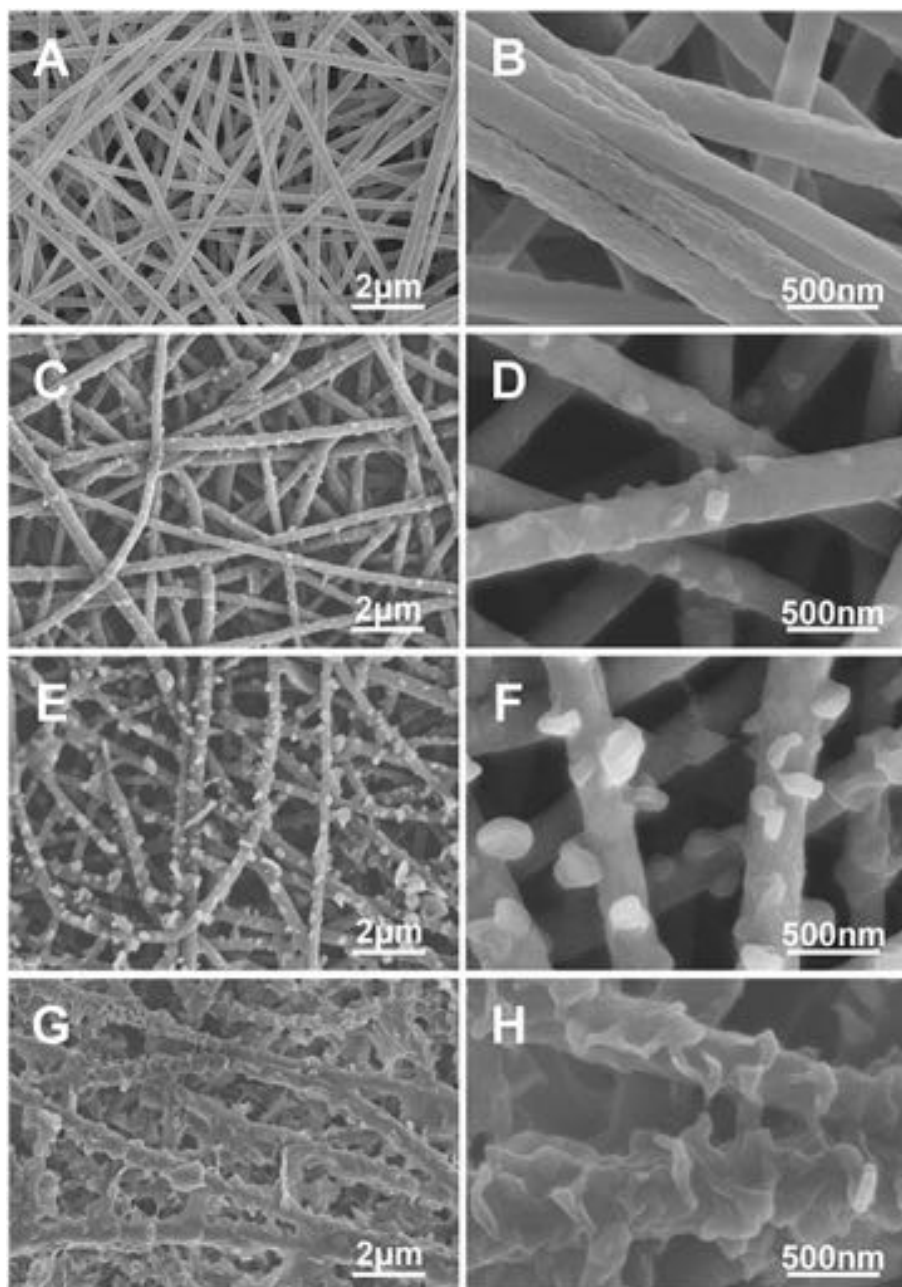


Fig. 12. FESEM images of different magnifications of (A, B) PVDF, (C, D) PVDF with 0.5% FTCS, (E, F) PVDF with 2% FTCS, and (G, H) PVDF with 3.5% FTCS. Images are reproduced with permission from Elsevier [58].

and superhydrophilic-omniphobic, in-air superhydrophilic and underwater superoleophobic outer skin layers are typically deposited onto hydrophobic or omniphobic porous substrates via dip-coating and/or plasma treatment to form fouling- and wetting-resistant Janus MD membranes. Novel configurations such as superhydrophilic-hydrophobic-hydrophilic and superhydrophilic-superhydrophobic-hydrophobic have been developed in recent years to enhance the robustness and permeation flux of Janus MD membranes. A typical example of a conventional Janus MD membrane is shown in Fig. 14. Through asymmetric surface-modification, Janus MD membranes can be endowed with fouling- and wetting-resistant properties for robust long-term performances in surfactant- and oil-containing feed streams. However, in order for Janus MD membranes to deliver effective performances, the selected substrate material ought to have a narrow pore size distribution so as to prevent complete hydrophilization of the substrate pores during the modification process.

Hitherto, the most common approaches to engineering Janus MD membranes are via dip-coating and/or plasma treatment. Zuo and Wang combined plasma grafting of polyethylene glycol (PEG) and dip-coating of titanium dioxide (TiO_2) nanoparticles to create in-air superhydrophilic surfaces [69]. The hydrophilic surfaces were observed to show lower affinity for oil droplets in the feed as compared to the hydrophobic surfaces of the virgin PVDF membranes. Furthermore, neither fouling nor wetting was observed after a day of operation, and this could be attributed to the benefits of reduced hydrophobicity of the modified membrane surfaces as well as smaller pore sizes after surface-modification. At certain pH levels where surface charges of the membranes and oil droplets were opposite, severe fouling was observed. This validates the point that there exists an important relationship between membrane surface chemistry and the feed.

Lin and coworkers demonstrated the potential of a novel approach by depositing agarose hydrogel layers on hydrophobic PTFE substrates

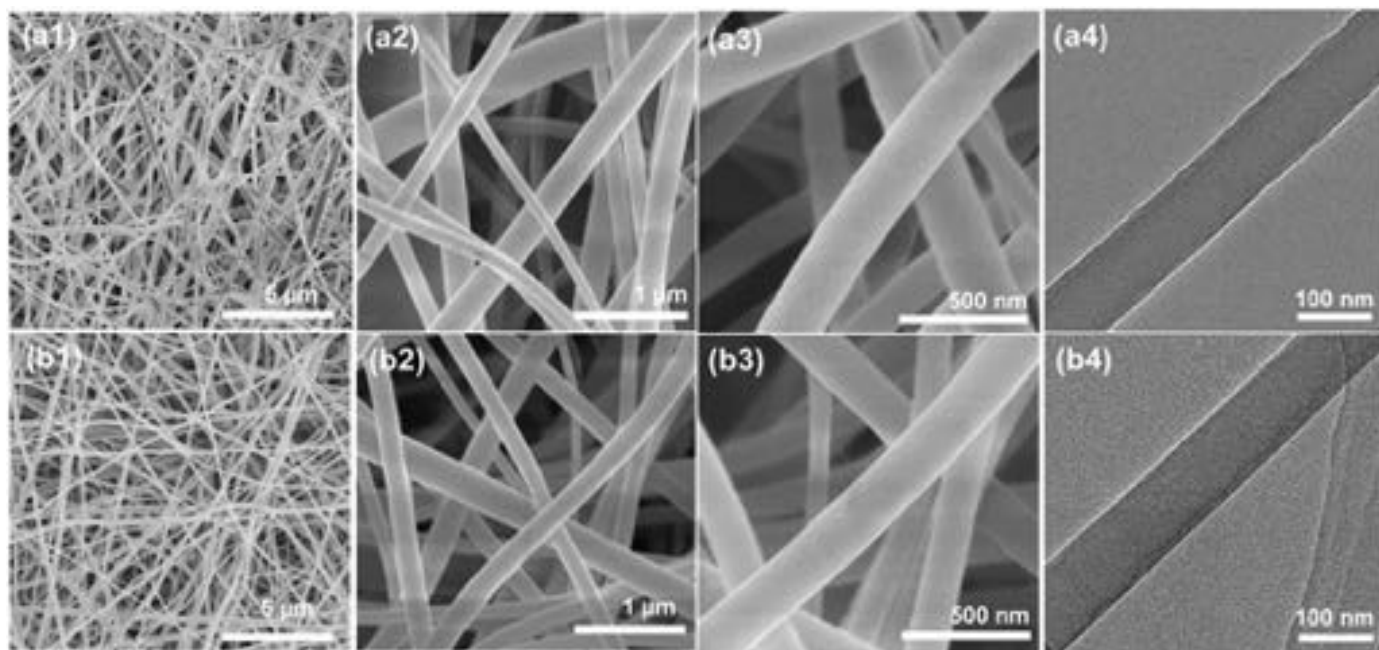


Fig. 13. SEM images of different magnifications of (a1, a2, a3) pristine PVDF-HFP and (b1, b2, b3) F-POSS/PVDF-HFP membranes. Transmission electron microscopy (TEM) images of (a4) pristine PVDF-HFP and (b4) F-POSS/PVDF-HFP membranes. Images are reproduced with permission from Elsevier [62].

[70]. The Janus MD membranes were able to prevent wetting in SDS and Tween® 20 solutions during 24 h of test duration. Even though deposition of the hydrogel layers resulted in a slightly lower flux than the pristine PTFE membranes because of the apparent increase in mass and heat transfer resistances, it led to prolonged robust performance in surfactant-containing dyeing wastewater. This was possible because of the static water layer that formed on the agarose hydrogel. This in turn caused surfactant unimers to orientate their hydrophilic heads towards the hydrogel layer whereas their hydrophobic tails remained outside, thus effectively preventing the penetration of surfactant unimers through the hydrogel layer as illustrated in Fig. 15. However, Lin et al. cautioned against the possible penetration of surfactant micelles, albeit occurring at a slow rate, into the hydrogel layer when the concentration of surfactants in the feed solution is above its CMC. These results were in good agreement with a recent study conducted on PDDA/poly(acrylic acid) (PAA) semi-interpenetrating hydrogel on a PVDF support [71].

Wang et al. demonstrated the potential Janus MD membranes for oil-containing feed waters by coating a combination of SiNP, chitosan (CTS) hydrogel, and fluoropolymer on commercial hydrophobic PVDF membranes [38]. The newly-developed Janus MD membranes exhibited underwater superoleophobicities, presenting very high oil contact angle values of close to 150°. These tailored membranes maintained a stable flux with high salt rejection rate throughout 36 h of test duration, which was ascribed to the interfacial hydration layer formed as a result of the interaction between hydrogen forming functional groups and surrounding water molecules in the emulsion. Similar to the study conducted by Lin et al. [70], Wang and coworkers also observed relatively lower flux for the modified membranes due to some pore blockages brought about by surface-modification and enhanced temperature polarization effect.

Designing different surface charges on the feed-facing surfaces of Janus MD membranes can lead to significantly different performances in charged emulsions [72]. Janus MD membranes with the same surface

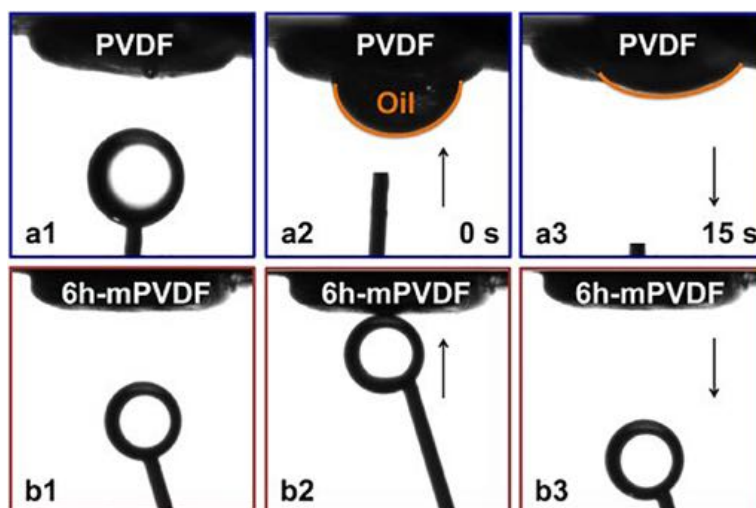


Fig. 14. Underwater interactions between an oil droplet and different membrane surfaces: (a1, a2, and a3) a hydrophobic membrane surface (PVDF) and (b1, b2, and b3) a Janus membrane surface (6 h-mPVDF). Images are reproduced with permission from Elsevier [24].

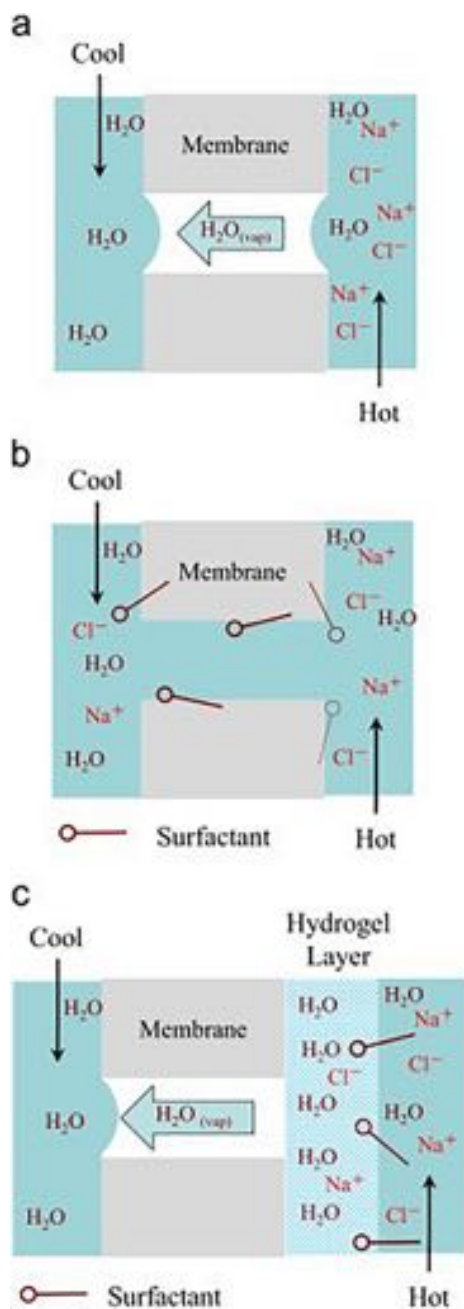


Fig. 15. Mechanisms of hydrogel layer against surfactant wetting: (a) MD before wetting; (b) MD after wetting; and (c) MD with protective layer. Images are reproduced with permission from Elsevier [70].

charge as the emulsion (positive-positive or negative-negative) produce stable flux and high salt rejection rate due to repulsive electrostatic interaction. On the other hand, opposing charges between the emulsion and the Janus membrane surfaces (positive-negative or negative-positive) lead to severe fouling because of attractive electrostatic interaction. A recent study has demonstrated the potential of zwitterionic coatings that endows Janus MD membranes with fouling- and wetting-resistant properties for enhanced performances in O/W emulsions with different charges [73]. Endowing Janus MD membranes with varying amounts of low-surface-energy functional groups also has a significant impact on the fouling-resistant properties of these membranes [74]. The presence of low-surface-energy functional groups on the modified membrane surfaces leads to anti-fouling behaviors. This is possible because these low-surface-energy functional groups could promote the detachment of foulants from membrane surfaces in

the presence of localized perturbation in the feed stream. However, a surplus of low-surface-energy moieties could have an adverse impact on membrane performances due to an increase in hydrophobicity, which could diminish the beneficial effects of the interfacial hydration layer.

To ensure that coatings on Janus MD membranes do not detach during continuous operations, more robust coatings need to be developed. Drawing inspiration from the excellent adhesive strength of mussels' byssus threads, Chew et al. developed Janus MD membranes through single-step co-deposition of mussel-inspired polydopamine (PDA) and polyethylenimine (PEI) on the outer surfaces of commercial hydrophobic PVDF membranes [23]. The modified membranes exhibited promising wetting-resistant properties against different surfactant types (non-ionic, anionic, and cationic) and excellent fouling-resistant properties against non-ionic (Tween® 20) and cationic (dodecyltrimethylammonium bromide, DTAB) surfactants. In addition, a stable flux with excellent distillate quality was maintained in an O/W emulsion during 168 h of test duration. Even though the modified membranes showed robust long-term performances in surfactant- and oil-containing feeds, the entire coating process was time-consuming and the deposited layers presented limited hydrophilicity. Considering the fact that dopamine polymerization is an oxidative process, Chew and coworkers made improvements to the previous method in a separate study by depositing PDA on both the outer and inner surfaces of the PVDF substrates in the presence of a strong oxidant, namely sodium periodate [24]. This improved method managed to shorten the coating duration significantly, and brought about improved in-air hydrophilicity to the deposited layers. The 'membranes' robust long-term performances could be alluded to the efficacious combined effects of the interfacial hydration layer and rough hierarchical structures as shown in Fig. 16. According to the Wenzel theory, the presence of rough surface structures renders a hydrophilic surface even more hydrophilic [41]. The interfacial hydration layer represents a significant energetic barrier for oil droplets and surfactant unimers to overcome in order to be attached onto the modified membrane surfaces [75]. It also serves as a protective layer to the membrane pores against surfactants and oils. The thickness of the deposited layers in Janus MD membranes determines the 'membranes' robustness and water recovery rate. A thinner layer delivers higher flux but is also prone to membrane fouling and pore wetting in the long run [76]. These novel Janus MD membranes with the superhydrophilic-hydrophobic configuration led to a flux enhancement of approx. 70% in 3.5 wt% NaCl solution at 333 K, ascribing to the favorable polar-polar interactions between vapor molecules and deposited polar functional groups on the modified membrane surfaces. In addition, because of the strong adhesive strength of dopamine coatings, the deposited layers remained structurally robust even after being subjected to ultrasonication. In their latest study, Chew et al. discovered that the creation of multilevel hierarchical structures on Janus MD membranes could pave the way for a new generation of fouling- and wetting-resistant MD membranes [25]. Multilevel hierarchical structures create a larger percentage of solid-liquid interfaces on the lyophilic side of Janus membranes, which in turn forms a very stable interfacial hydration layer that prevents the attachment of surfactants and oils.

Recently, researchers have begun exploring into the development of Janus MD membranes with the superhydrophilic-omniphobic configuration as this configuration combines the fouling-resistant properties of superhydrophilic surfaces and wetting-resistant properties of omniphobic membranes as mentioned in the previous section [77]. These novel Janus membranes have shown to be able to resist wetting by SDS unimers. They also maintained a stable flux with excellent distillate quality in an O/W emulsion. These results are certainly promising but their performances in long-term tests still require validation. Janus membranes formed via in-situ reactions or pressurized spraying techniques might lead to pore defects during the modification process and subsequent pore wetting during operations [78,79]. To overcome

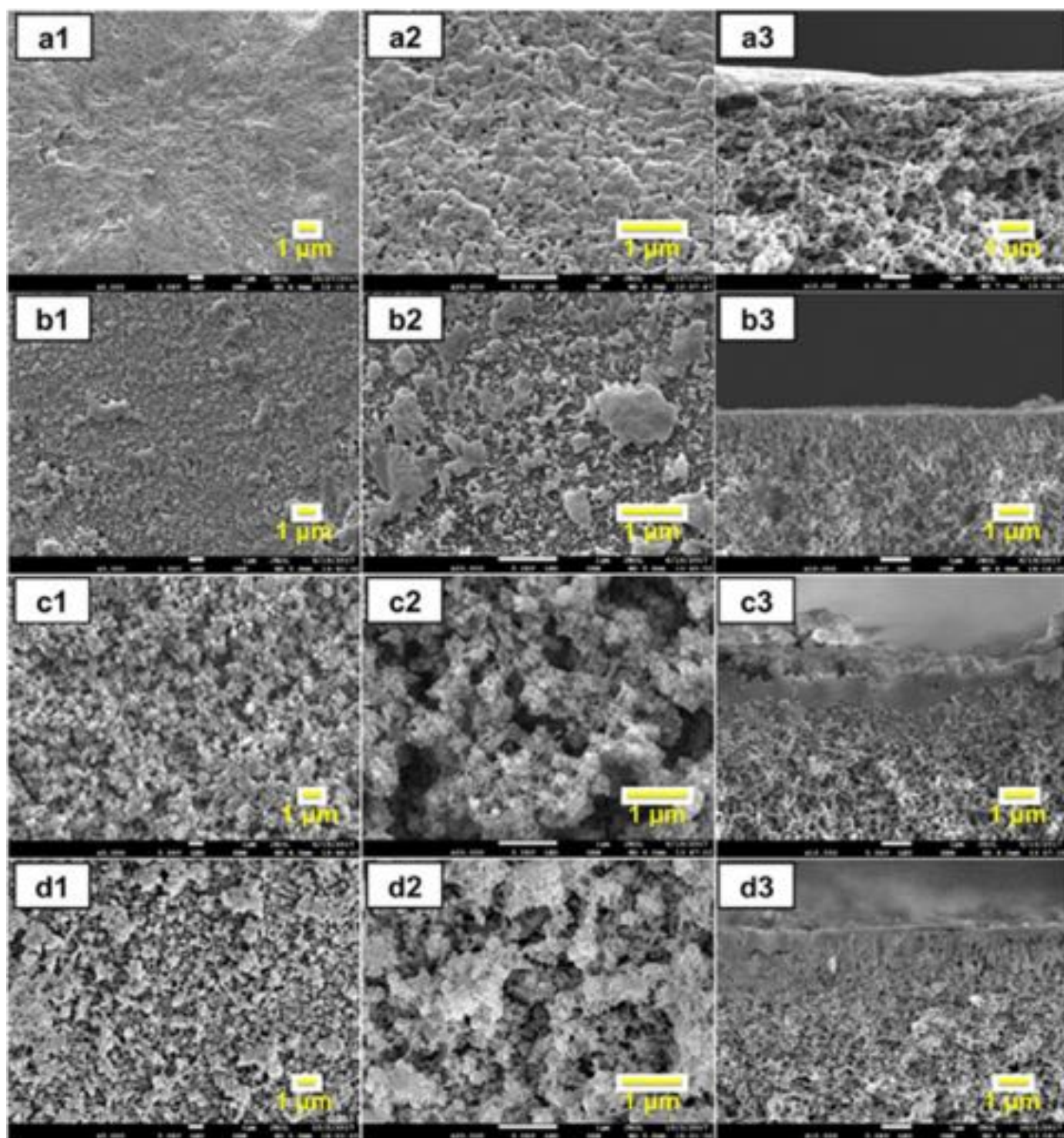


Fig. 16. FESEM images of the outer surface morphologies of the hydrophobic membrane (a1 and a2), Janus membrane with 2 h coating (b1 and b2), Janus membrane with 6 h coating (c1 and c2), and ultrasonicated Janus membrane (d1 and d2). FESEM images of the cross-section morphologies of the hydrophobic membrane (a3), Janus membrane with 2 h coating (b3), Janus membrane with 6 h coating (c3), and ultrasonicated Janus membrane (d3). Images are reproduced with permission from Elsevier [24].

potential pore wetting in long-term operations, the formation of an underwater superoleophobic fibrous network of cellulose acetate (CA) and SiNP via electrospinning on commercial PTFE membranes was proposed [78]. This type of Janus MD membrane possesses a top layer with highly porous and interconnected surface structures that could minimize additional resistance to vapor transport. These newly-engineered Janus membranes demonstrated fouling-resistant property in an O/W emulsion during 30 h of test duration. Oil stains on the Janus membrane

surfaces could be washed off easily by rinsing with deionized water as shown in Fig. 17. These results were in good agreement with a similar study conducted by Wang et al. [80]. While this novel electrospinning technique to engineer Janus membranes has proven to work well on flat-sheet membranes, it might not be economical and applicable to hollow fiber membranes. This is because a uniform deposited layer on hollow fiber membranes would be unrealistically difficult to achieve by deploying this technique. Another novel technique of fabricating Janus

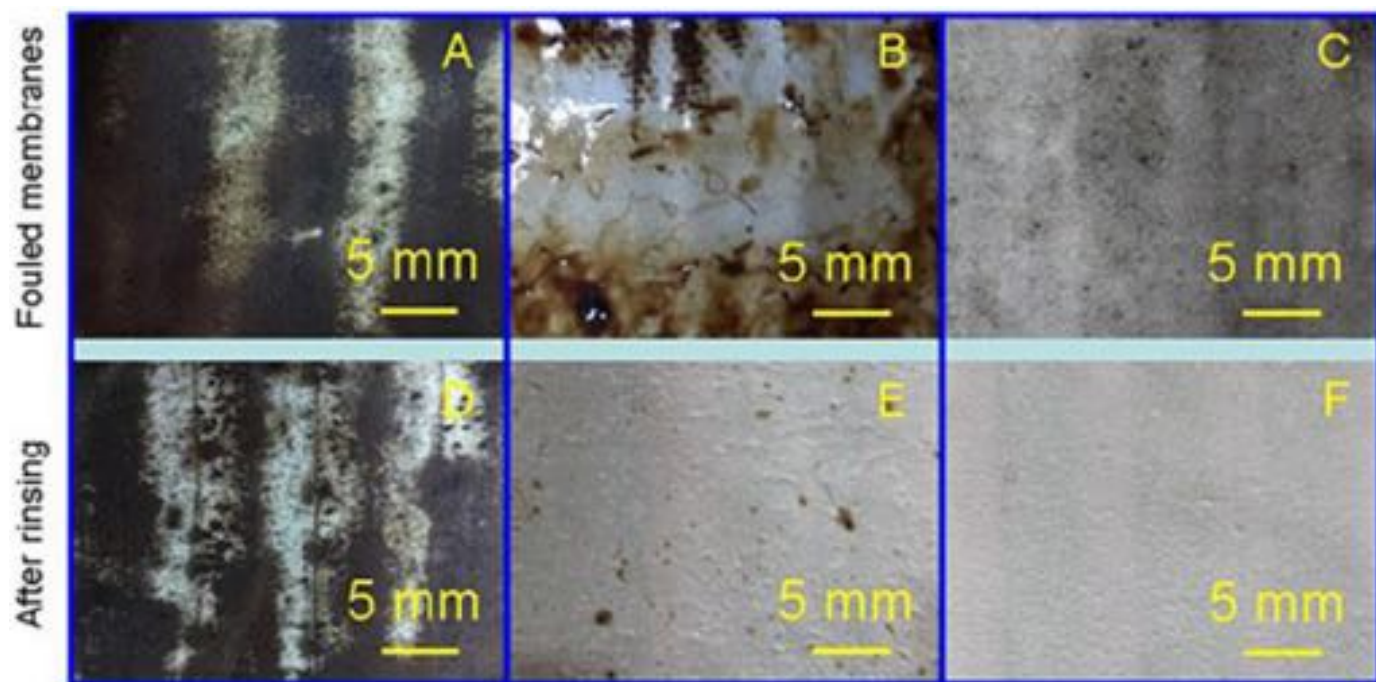


Fig. 17. Photographic images of the different membranes after DCMD experiments, and the photographic images of the fouled membranes after rinsing with deionized water for 2 min. (A) and (D) commercial PTFE membranes; (B) and (E) PTFE/CA composite membranes; and (C) and (F) PTFE/CA/SiNP composite membranes. Images are reproduced with permission from Elsevier [78].

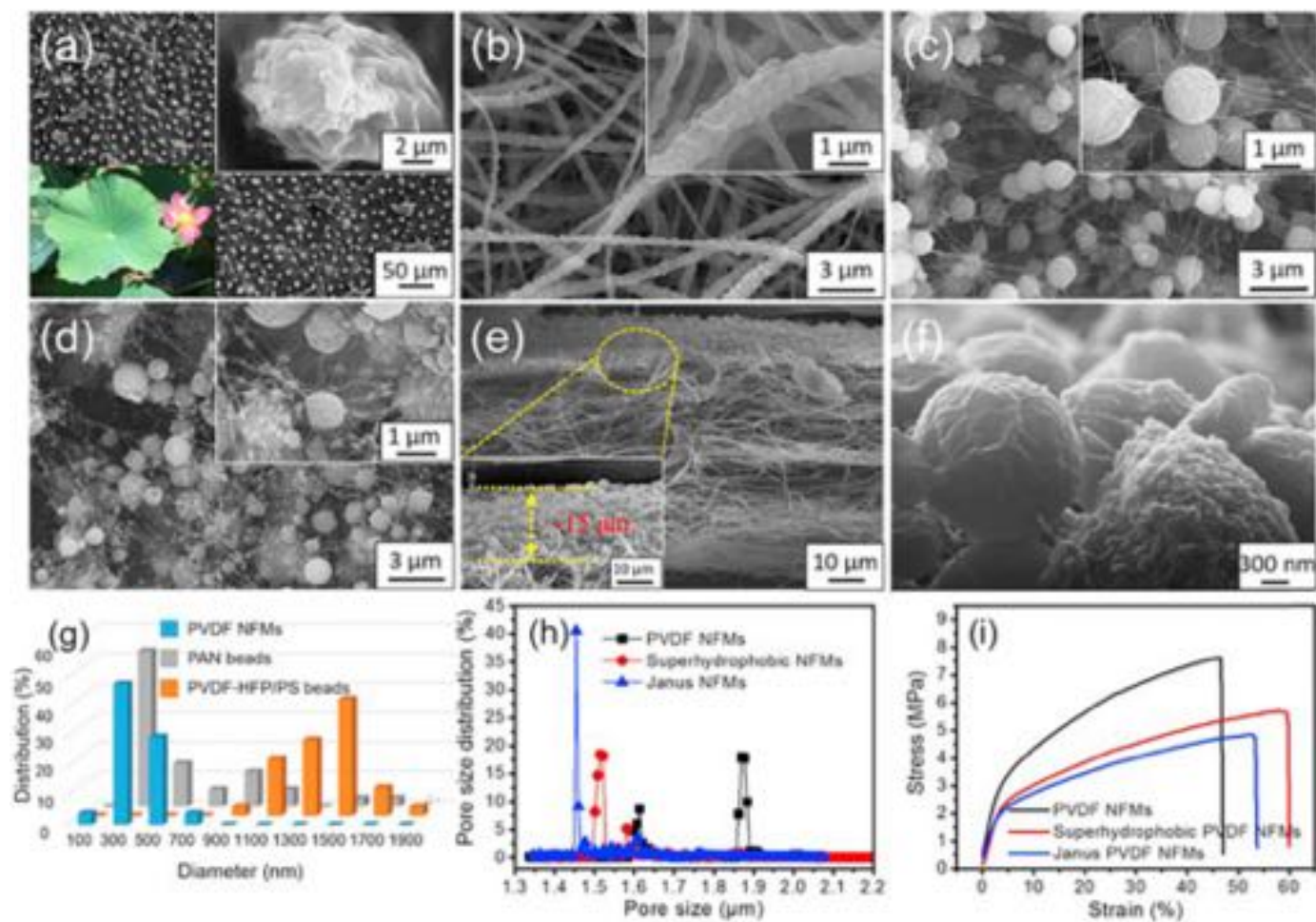


Fig. 18. Morphology, pore structure, and mechanical strength of the Janus membrane. (a) Photograph and enlarged FESEM images of a lotus leaf. (b) FESEM image of the necklace-structured PVDF substrate. FESEM images of the Janus skin layer with asymmetric superwettability: (c) the superhydrophobic layer and (d) the superhydrophilic layer. (e) Cross-sectional image and (f) enlarged image of the top layer of the Janus membrane. (g) Fiber and microspheres diameter distributions of the corresponding Janus membrane. (h) Pore size distribution and (i) mechanical strength of the Janus membrane at each stage of fabrication. Images are reproduced with permission from Elsevier [82]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

MD membranes with the superhydrophilic-omniphobic configuration is via the surface-initiated atom-transfer radical-polymerization (ATRP) technique [12]. Li et al. demonstrated grafting zwitterionic polymer brush layers that displayed underwater superoleophobic properties on omniphobic substrates with multilevel re-entrant structures that remained robust in surfactant solutions and O/W emulsions.

The development of Janus membranes for surfactant- and oil-containing feed waters is certainly an interesting strategy to prevent membrane fouling and pore wetting in long-term MD operations. However, conventional surface-modification techniques such as polymerization deposition and spray-coating generally reduce the permeation fluxes of Janus membranes because of their uncontrollable operations and partial pore blockages. Therefore, it is of paramount importance to explore novel techniques to optimize the thicknesses of the deposited superhydrophilic layers and/or their accompanying pore size distributions in order to deliver competitive permeation fluxes while insuring that distillates of excellent quality are produced [81]. Recent works have provided an insight into this. Zhu and coworkers invented novel triple-layer Janus MD membranes (superhydrophilic-superhydrophobic-hydrophobic) with competitive fluxes for oil-containing wastewaters by integrating breathable and asymmetrically superwetable ultrathin skin layers on hydrophobic nanofibrous membranes as illustrated in Fig. 18 [82]. The Janus membranes exhibited underwater superoleophobicity and in-air superhydrophobicity properties due to the formation of hydration layer and air pockets on the respective skin layers. They delivered permeation fluxes that were comparable to those of pristine PVDF membranes, and remained robust during treatment of an O/W emulsion for 30 h of test duration. This novel technique of fabricating Janus membranes is certainly promising, and has the potential to be applied for a wide range of MD applications.

As illustrated in Fig. 19, performing pore channel surface modification has been proposed as an alternative to prevent the increase in mass transfer resistance brought about by the deposition of

superhydrophilic layers in Janus MD membranes [83]. Graphene oxide (GO) particles were deposited on the internal surfaces of the membrane pores via a dynamic forming process. As compared to the pristine PVDF membranes, the GO-based Janus membranes demonstrated reasonably good fouling- and wetting-resistant properties in an anionic surfactant solution (sodium dodecyl benzene sulfonate, SDBS) during 5 h of operation, which was ascribed to the presence of oxygen-containing functional groups and the healing of membrane pore defects. While the pore channel surface-modification strategy looks promising, it is worth noting that optimization of the deposition conditions (time and depth) and particle loading are extremely important in preventing pore wetting. These results would have been of more value had comparison tests been carried out against an individual external layer formed by GO particles instead of SiNP.

In a recent study conducted by Garcia et al., it was highlighted that the use of traditional membrane cleaning chemicals such as sodium hydroxide (NaOH) might not be suitable for Janus MD membranes [84]. Wetting was observed for the Janus membranes, as evidenced by a rise in permeate conductivity after cleaning with 1 wt% NaOH. The results suggest that a set of cleaning protocols targeted specifically at Janus membranes needs to be established to ensure sustainable MD operations.

As reviewed thus far, Janus membranes for MD applications are typically manufactured through asymmetric surface-modification since it offers greater flexibility in manipulating the surface properties of available pristine substrates [85]. Nevertheless, asymmetric surface-modification remains a challenging technique for porous substrates due to potential wicking or complete hydrophilization of the substrate pores during the modification process. This is why the selection of suitable substrates, such as omniphobic substrates, and development of novel interfacial strategies are critical in this technique. The thickness ratio between the hydrophilic and hydrophobic layers in Janus membranes determines the

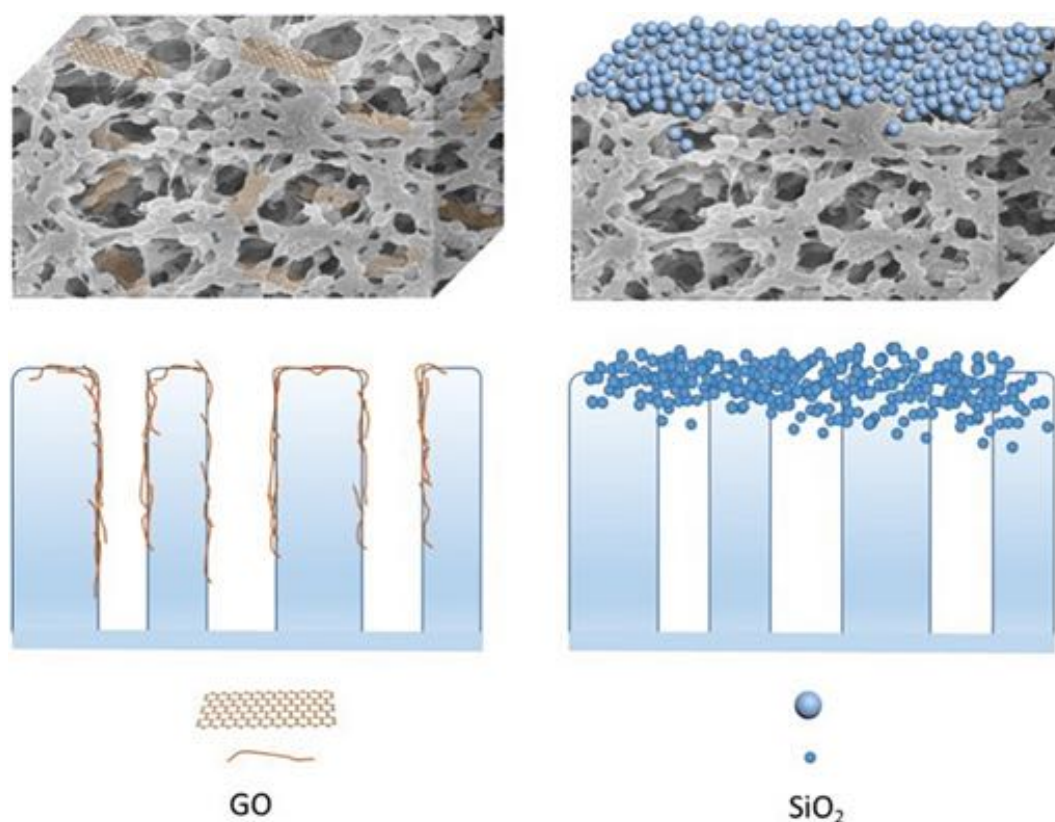


Fig. 19. Schematic diagram of pore channel surface modification with GO and external surface modification with SiO₂. Images are reproduced with permission from Elsevier [83].

robustness and transport properties of these membranes. Due to difficulties in precisely adjusting the thicknesses of the deposited layers in Janus membranes, these membranes often suffer from lower permeation fluxes as compared to pristine substrates. Therefore, more focus needs to be directed towards optimizing surface structures and understanding transport mechanisms of Janus MD membranes for surfactant- and oil-containing feed streams. The attachment of amphiphilic polymers on conventional surfaces to create hygro-responsive membranes could be another viable option. Hygro-responsive membranes are membranes with reversible and switchable wetting properties in both air and water. [86]. The technique used to fabricate hygro-responsive membranes is highly versatile and can be applied to different materials. More importantly, these membranes are capable of producing exceptionally high fluxes and separating emulsions into their oil and water constituents. Thus, hygro-responsive membranes are very promising candidates for water recovery from high-salinity feed streams that contain surfactants and oils. Finally, the stability between the asymmetric layers in Janus MD membranes needs further reinforcement to withstand standard membrane-cleaning protocols in ensuring sustainable long-term operations.

4. Conclusions and outlook

Membrane fouling and pore wetting encountered in low-surface-tension feed streams are key challenges limiting practical implementation of the MD process for niche applications as these phenomena more often than not lead to an undesirable loss in permeation flux and/or selectivity. In this critical review, we have examined different synthesis routes that endow membrane surfaces with bespoke structures and wettabilities, and detailed how further improvements in future membrane designs could be even more effective in mitigating membrane fouling and pore wetting. However, for MD to potentially be competitive as a technology for desalinating high-salinity brines that contain surfactants and oils, an in-depth understanding of the influences of these contaminants on membrane fouling and pore wetting as well as any underlying mechanisms must first be realized before better guidelines and strategies can be developed for future bespoke membrane designs that could deliver superior and economical performances.

The development of omniphobic and Janus MD membranes has been deemed revolutionary in dealing with difficult feed streams. Current trends in membrane development for surfactant- and oil-containing feed streams have generally focused on the fabrication of novel membranes as well as the demonstration of enhanced performances such as fouling- and wetting-resistant properties against various low-surface-tension media. The possibility of scaling-up has hitherto been neglected. Consequently, complex preparation methods that more often than not drive production costs up have been proposed, which further hinder practical implementation. Looking ahead, economical and facile innovative solutions that involve novel membrane materials and surface-modification techniques have to be designed with special emphasis placed on membrane scalability. In addition, we recommend that current as well as future MD membranes be subjected to and evaluated in long-term operations to ensure consistent performances in a myriad of applications. While most, if not all, surface-modified membranes inevitably possess relatively lower fluxes as compared to pristine substrates, researchers should continue in their pursuit for MD membranes with competitive or enhanced permeation fluxes by inaugurating trailblazing methods of performing surface-modification such as the creation of hygro-responsive membranes. For that to come to fruition, interdisciplinary collaborative efforts between materials scientists and 'membranologists' are crucial in developing the next generation of high-performance operationally-stable MD membranes for niche applications.

Author contributions

N.G.P.C. designed the manuscript, processed the references, prepared the original figures, and wrote the draft manuscript. S.Z. and R.W. contributed discussing and checking the final version of the manuscript.

Declaration of Competing Interest

None.

Acknowledgements

The authors would like to acknowledge funding support from the Singapore Economic Development Board to the Singapore Membrane Technology Centre.

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