



Cost-effective polymer-based membranes for drinking water purification

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Keywords: Polymer-based membranes, Drinking water purification, Membrane components

Global water scarcity is exacerbating owing to climate change and pollution, making the demand for clean water more challenging with the growth of the global economy and population. Membrane filtration technologies have been widely applied in drinking water purification due to their energy efficiency while facing challenges like fouling, degradation and trade-offs, such as selectivity and permeability. The sustainable development of our society demands further understanding and improvement of those membranes. In this review, the basic structures of polymer-based water purification membranes including the effective layer for separation, the support layer and the possible top protective layer are presented. Details include the conventional membranes for microfiltration (MF) and ultrafiltration (UF), the effective layers for separation in thin-film composite (TFC) membranes, electrospun nanofibrous membranes for MF, UF, and membrane distillation (MD), as well as the emerging self-assembled block copolymer membranes. Furthermore, the conventional support layers and electrospun nanofibrous support layers for reverse osmosis (RO) and forward osmosis (FO) processes, and the top protective layers are discussed. The materials, membrane structures and properties, modification strategies, possible interlayers, interconnects, interpenetration, and interactions between different layers are discussed, with the emphasis on the cost-effectiveness of various membranes.

1 Introduction

Waterborne diseases are a common health issue all over the world, which often result in a significant number of illnesses and deaths, especially if the quality of drinking water is poor. The purification of drinking water is an essential issue for the health of human beings. It is especially challenging in less developed countries. How water purification can be achieved efficiently and economically depends on the impurities in the water and whether

they could cause major health issues. There are a good number of different ways to obtain water with drinking quality, depending on what we look for in the water quality. The common pathways for water purification are as follows. (1) Distillation (including different boiling processes) is the traditional but expensive approach to obtaining pure water. At high temperatures, bacteria and viruses are killed and some soluble impurities (such as calcium carbonate) can be precipitated. However, the boiled water often needs to be strained before drinking. (2) Killing bacteria and viruses by adding iodine or chlorine. However, the taste of water may be affected. Alternatively, using UV light to kill bacteria and viruses can make water safe to drink. Sometimes water after treatments has been made to pass through coarse and fine sands to

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Received 4 February 2022; Received in revised form 25 March 2022; Accepted 25 March 2022

remove unwanted solids and/or smell. (3) In coastal areas, reverse osmosis has been applied to remove salts in seawater to obtain good quality drinking water.

The selection of a proper method of water purification depends on the type and properties of the major impurities that we want to remove, and the feasibility to achieve large-scale and economical purification. Common impurities in the water can be broadly classified as (1) undissolved impurities, such as suspended solids, inorganic or organic particles, and small microorganisms; (2) dissolved impurities, such as ionic or salt species and biological entities with ionic charges that can interact with water; and (3) gaseous impurities, such as hydrogen sulfide. When dealing with water purification, it is important to identify what the major impurities are and which species we want to take out in order to use water for a *specific* application. *The key emphasis deals with a cost-effective approach to achieve the objective.*

Membrane filtration is a broadly used technique in water purification. This review will focus on polymer-based membrane materials.

2 Basics of membranes for water purification

2.1 Isotropic and anisotropic membranes

The properties, performance, and applications of membranes for water purification are highly dependent on the structure and the materials used for the membranes. For synthetic membranes, there are two main categories: isotropic or symmetric membrane and anisotropic or asymmetric membrane (Fig. 1) [1].

Isotropic membranes, with a chemically homogenous composition, typically have three types: microporous membranes, nonporous dense membranes, and electrically charged membranes [2]. Isotropic membranes are used for separating molecules/particles that differ greatly in size, e.g., in microfiltration/ultrafiltration processes. The filtration process is

determined by a pore size distribution and the sizes of impurities. Impurities with sizes larger than the maximum pore size will be rejected, while small species can pass through the pores. Isotropic microporous membranes are widely used in the microfiltration process. A nonporous dense membrane allows water to be transported by diffusion under the driving of concentration, pressure, or electrical potential gradient. Therefore, these membranes are suitable for separating species with different solubility and diffusivity in the membrane material, for instance, in gas separation, pervaporation, and reverse osmosis processes. Electrically charged membranes typically have pore walls with negatively or positively charged ions in either microporous or dense frameworks. These membranes are usually utilized for electrodialysis, where the charged impurities will be attracted by the charged ions on the membrane walls and be retained within the membrane (Fig. 1).

Anisotropic membranes can be either chemically and/or structurally heterogeneous, which have two major types: Loeb and Sourirajan membranes [3] and thin-film composite (TFC) membranes [2]. Loeb and Sourirajan membrane consists of a single type of membrane material with pore size and porosity that differ in different layers [2]. The TFC membranes typically have a thin, dense surface layer for separation (the gray layer in the thin-film composite membrane in Fig. 1) and a thick, porous layer for mechanical support. The separation performance of TFC membranes is acknowledged to be dominated by the polyamide active layer, while recent studies demonstrated the negligible impact of the support layer on membrane performance [4–8].

Various techniques have been developed to fabricate water purification membranes. Isotropic membranes used in water filtration applications are often prepared by phase separation (i.e., phase inversion) techniques. [2] The first phase inversion membrane was developed by Loeb and Sourirajan in the 1960s, which was a high flux anisotropic reverse osmosis membrane made from cellulose acetate [3]. The Loeb and Sourirajan process is now acknowledged as a special case of the phase inversion process. Anisotropic membranes fabricated by the Loeb and Sourirajan technique consist of a single membrane material with gradient pore structures across the membrane cross-section. Other anisotropic membranes used on a large scale usually consist of layers with different functions. These membranes are often prepared by interfacial polymerization process and solution-coating process. Moreover, the emerging nanofibrous membranes with high separation performance, broad applications and low costs are mostly prepared by electrospinning, which is rapidly emerging as a facile and powerful technique to prepare smooth nanofibers with adjustable morphology and functionality from various polymers.

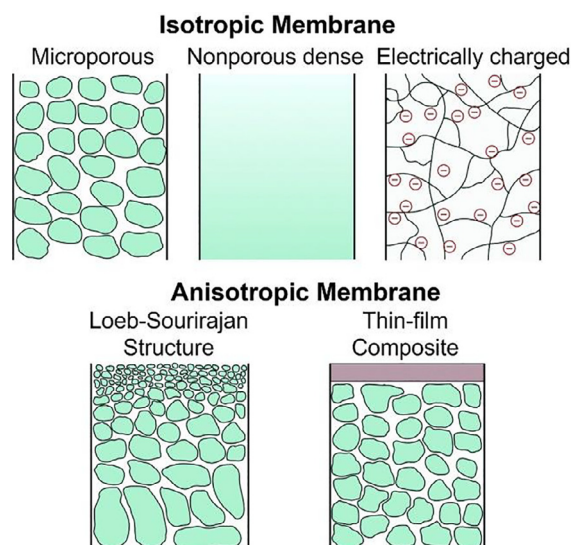


Fig. 1

Schematic representation of various isotropic membranes and anisotropic membranes. (The possible nonwoven fibrous substrate at the bottom is omitted for clarity.) Reproduced with permission from Ref. [1]. Copyright © 2016, Royal Society of Chemistry.

2.2 Classification of membranes

Membranes for water purification can be classified by different criteria. In terms of filtration mechanism, membranes are divided into pore-flow membranes and solution-diffusion membranes [2]. Based on filtration processes, membrane systems can operate either through dead-end filtration or cross-flow filtration. In terms of membrane modules, there are plate-and-frame modules, hollow fiber modules, spiral-wound modules, tubular modules,

and vibrating and rotating modules. According to contributing area of membrane structure, membranes can be screen filters or depth filters [9]. Based on pore size, membranes employ four classes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) as well as the emerging forward osmosis (FO). Among these categories, the category defined by pore size is the most widely used one, since pore size directly impacts the filtration for specific impurities.

MF membranes possess pores with sizes of 0.1–5 μm , which has been widely used for drinking water purification. MF membranes can remove particles, asbestos, and waterborne bacteria with the size of 0.1–10 μm in diameter under low operating pressure (< 2 psi or by gravity) [10]. MF membranes usually operate exclusively by the pore-flow mechanism. UF membranes have smaller pore sizes ranging between 0.01 and 0.1 μm , which can remove dissolved bio-macromolecules, such as proteins, viruses, and pyrogens. Thus, UF has a wide range of applications for industrial and community wastewater treatment. The common operating pressure of UF membranes is 10–30 psi. Usually, UF membranes possess an anisotropic Loeb and Sourirajan structure and operate on a pore-flow mechanism [1]. NF membranes are applied for species with sizes ranging from 0.001 to 0.01 μm , such as multivalent ions (e.g., magnesium, calcium, lead, and chromium,) and surfactants. NF membranes follow a combination mechanism of pore-flow and solution-diffusion [9], and usually operate under a pressure of 100 psi.

Compared with MF, UF and NF membranes, RO membranes are considered essentially non-porous (pore size approx. < 1 nm) [1]. RO membranes operate on a solution-diffusion mechanism [2], that solutes cross the membrane by dissolution in the membrane matrix and subsequent diffusion under applied pressure. Generally, RO membranes are utilized for the desalination of brackish groundwater and seawater. Therefore, these membranes are supposed to meet four requirements: (i) high water permeability and high salt rejection rate; (ii) thin membrane layer with sufficient mechanical integrity; (iii) high area per unit volume; (iv) chemical and physical stability [9]. Cellulose acetate-based membrane and polyamide TFC membrane are the two main types of RO membranes nowadays, while the latter currently dominate the commercial RO membrane market [11,12]. RO membranes operate under high pressures of 150–1000 psi, while FO membranes function by the drive of the osmotic pressure difference between a diluted feed solution and a more concentrated draw solution. FO has a low fouling propensity, high rejection rate, and a capacity for high osmotic pressure driving forces that surpass the operating limitation of RO, making FO a good choice as a pretreatment step to enhance water quality and system recovery for conventional desalination operations [13].

2.3 The State-of-the-art of membranes for water purification

To purify natural water sources, such as lakes and rivers, into drinking water quality, membrane-based treatment technologies are favored for the removal of the impurities and contaminants from industrial and agricultural wastewater due to their advantages in simplicity, energy efficiency, manufacturing scalability, and small footprint. However, these membranes are

generally subject to an inherent trade-off between selectivity and permeability [14], as well as some practical challenges, such as fouling and degradation. The trade-off between membrane permeability and selectivity has raised intense discussions in recent years, with reference to an increase in water permeability and a deterioration of selectivity of impurities [15]. For porous membranes, the trade-off greatly impairs filtration performance, while an increase in water permeability without losing selectivity can be achieved by increasing surface porosity and/or decreasing the active layer thickness. For non-porous membranes, such as TFC membranes, the impact of the trade-off on membrane performance is eliminated possibly because of the polymer network structures and dense film morphologies [14]. For all membrane systems, fouling is the major challenge for efficient operation, which leads to a greatly reduced membrane performance and higher cost. Fouling and other performance issues will be discussed in the following sections.

To address those obstacles and to improve performance, membrane filtration technologies for water purification have been advancing toward two main developmental directions in recent decades: (1) to find or create new advanced materials with high durability and good filtration properties in order to fabricate cost-effective and environment-friendly membranes; (2) to optimize or to design morphology and structure of membranes for high filtration efficiency [10,14]. A schematic diagram, as given in Fig. 2, displays the two directions and indicates the outline of this review.

In the matter of materials, organic (polymeric), inorganic, and organic-inorganic hybrid materials have been studied as membrane materials for water purification. Polymeric membranes possess good chemical resistance, mechanical properties, and flexible processibility, making cost-effective polymers the most widely used materials. Typical polymers for membrane filtration include polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyethersulfone (PES) and polysulfone (PSF). Self-assembled block copolymer membranes have been explored as potential membranes with enhanced properties [14]. Membranes made from inorganic materials such as zeolites, ceramics, glass, and metals, exhibit excellent properties for water filtration, whilst their high cost, complex fabrication process, and environmental concerns have limited their commercialization [16]. Moreover, the introduction of (nano-sized) organic/inorganic additives into the polymeric membrane is among the most popular designs for membrane performance enhancement. The fillers dispersed in diverse positions can form composite/nanocomposite with the polymer matrix, leading to significant enhancement of hydrophilicity, water permeability, rejection rates, and antifouling properties, as well as mechanical strength [17]. Aside from conventional polymeric membranes, electrospun nanofibrous membranes have offered a much more efficient, cost-effective, and scalable approach for water purification.

Regarding membrane structure and morphology, the TFC membrane is a practical model for efficient membrane filtration. Polyamide TFC membranes are the gold standard for NF, RO and FO operations [18]. Electrospun nanofibrous scaffolds have the potential to serve as an alternative for the conventional support layers in TFC membranes and to form thin-film nanofibrous

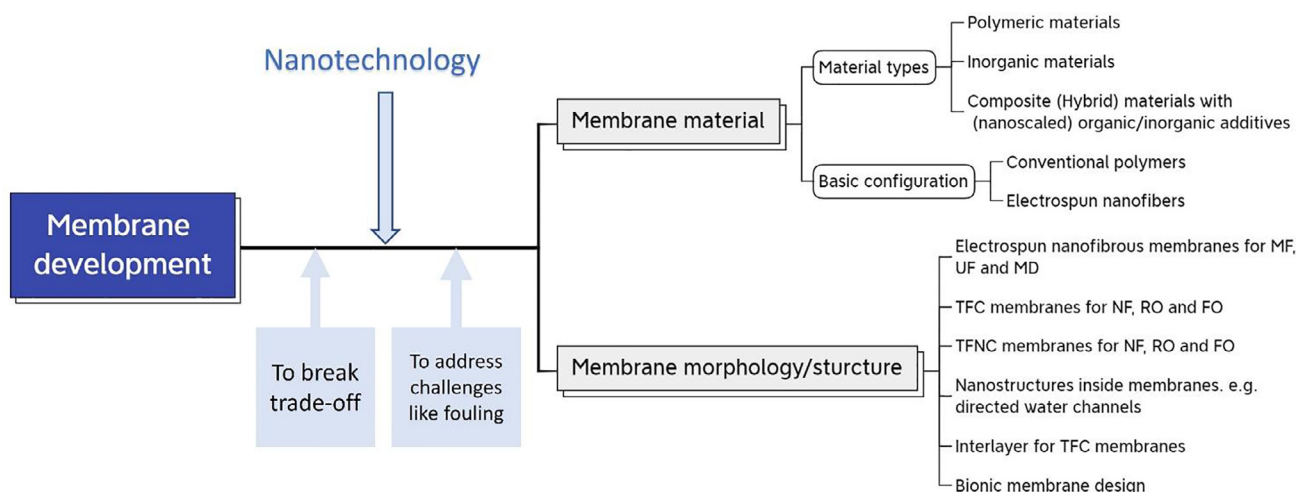


Fig. 2

Schematic diagram of recent development of cost-effective membranes for water purification.

composite (TFNC) membranes with unique properties, such as high porosity and interconnected pores [4]. These properties enable TFNC membranes to have higher permeability and lower energy consumption costs than traditional TFC membranes [19]. An introduction of an interlayer between the polyamide layer and the support layer in TFC membrane systems was also proposed to increase permeability and antifouling property. Inspired by nature, such as the lotus leaf effect [20,21], some biomimetic membranes have been modified into specific morphologies and structures with good performance [22]. In addition, the studies of nanostructures inside the membrane systems, such as directed water nanochannels, also promote the development of membrane technology.

In this review, we discuss the progress from a perspective of membrane components, that is the effective layer that does separation, the support layer as well as a possible top protective layer.

3 Effective layer for separation

3.1 Conventional MF and UF membranes

Microfiltration and ultrafiltration are related processes with pore sizes as the major distinction. Isotropic microporous membranes are widely used as MF membranes, while UF membranes are usually made by the Loeb and Sourirajan process and have anisotropic structures consisting of a finely porous surface layer or skin and a relatively open microporous substrate [2]. Since most of the conventional MF and UF membranes consist of a single membrane layer and/or are prepared by a single-phase separation process, in this review, we treat the MF and UF membranes as the “effective layer for separation” to discuss.

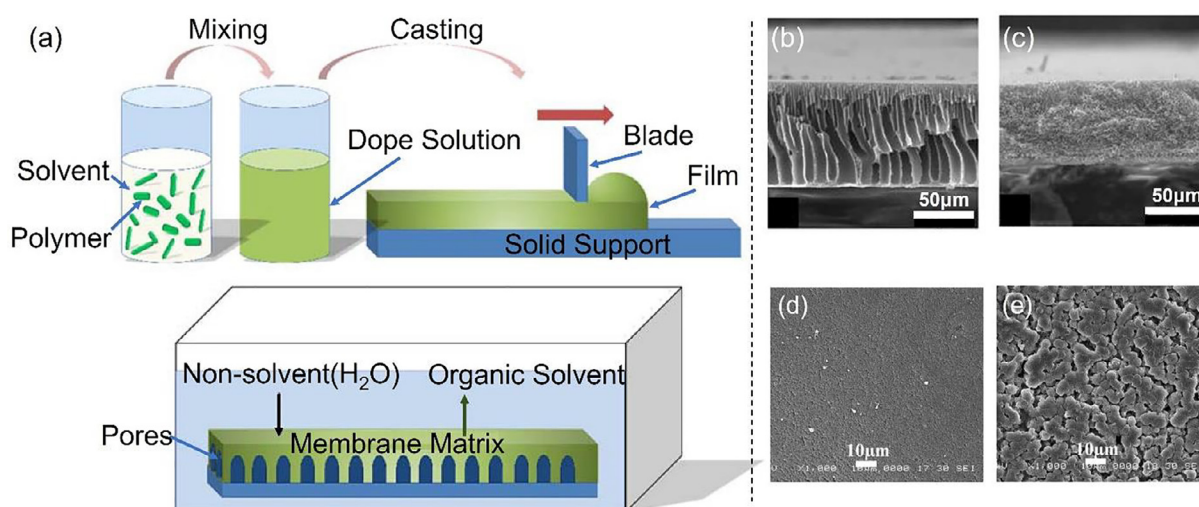
The main phase inversion technique, i.e., the non-solvent-induced phase separation (NIPS) [23], involves the immersion of a film, made from the polymer solution, into a non-solvent bath (usually a water bath), thereby causing phase separation. Ultimately, the polymer-poor phase forms the pores, while the polymer-rich phase constructs the solid membrane matrix (Fig. 3a) [24]. A variety of factors, including intrinsic features of polymers,

solvents, polymer concentration and fabrication techniques, can lead to multiple varieties of final membrane morphology. For example, some asymmetric/symmetric membranes are shown in Fig. 3b–e [25,26].

Cellulose acetate (CA) membrane for water purification was first studied by Reid and Breton [27]. With high salt rejection properties, hydrophilicity, cost-effectiveness, flexibility in processing, and non-toxicity, CA membranes still serve as one of the most commonly used membranes for water filtration nowadays. Nevertheless, CA membranes suffer from several drawbacks, including low thermal, chemical and biological stability, narrow functional pH (2–8) and temperature ranges ($< 30\text{ }^{\circ}\text{C}$) [1,28]. Many strategies have been developed to make up for the deficiencies and enhance separation performance: blend CA with other hydrophobic polymers to fabricate mixed matrix membranes, such as CA/PU [29], CA/PVA [30], CA/PEI; [31] incorporate nano-fillers like carbon nanotubes [32] or TiO_2 [33].

PVDF exhibits high mechanical strength, thermal stability, good chemical resistance and a long lifetime, as well as good flexibility and processability for fabricating into different modules. These properties make PVDF a favorable material for MF and UF membranes, and also for the support layer for NF and RO membranes. The applications have been summarized in several reviews [34–37]. Other polymeric materials favorably applied for MF and UF processes include PSF [38], PES [39], PAN [40], polyamide (PA) [41], polytetrafluoroethylene (PTFE), and polypropylene (PP) [42], some of which can also be used as substrates or as pretreatment membranes for NF and RO operations.

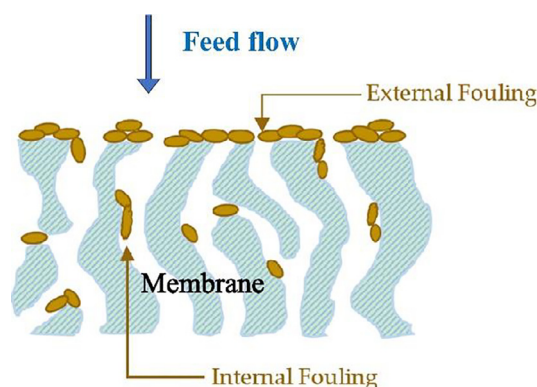
Membrane fouling is the critical obstacle for the implementation of pore-flow filtration, which leads to higher costs (to clean or replace membranes) and degeneration of filtration performance [43]. Fouling is the accumulation of solid particulates, micro-biological organisms, organic dissolved components/colloids which tend to be absorbed by the membrane, or/and inorganic dissolved components which

**Fig. 3**

(a) Schematic illustration of conventional phase inversion process; (b, c) Cross-section SEM images of PES MF membranes with finger-like voids and sponge-like structures, respectively; (d, e) top-view SEM images of PVDF membranes with continuous skin surface and irregular porous surface, respectively. Adapted with permission from Refs.[24–26]. Copyright © 2016, Springer-Verlag Berlin Heidelberg and © 2007 Elsevier B.V. All rights reserved.

tend to precipitate [44]. The fouling rate is related to the nature of the filtration membranes, such as surface properties and surface volume ratio, water flux and feed concentration [45]. Porous membranes experience two types of fouling: surface fouling (external fouling), caused by deposition of particulates on the membrane surface that reversibly consolidate over time; internal fouling, generated by the penetration of solid impurities, which is usually irreversible (Fig. 4) [46]. Among several proposed fouling mechanisms [47], concentration polarization appears to be the one effect being considered most often [48–50]. Compared with membrane cleaning and replacement, developing robust membranes with antifouling properties is the most fundamental strategy which can be cost-effective and can maintain/improve filtration performance [51].

Hydrophilic surface construction is the most common approach to building antifouling membranes. It can be achieved by two types of approaches: 2D modification, which mainly

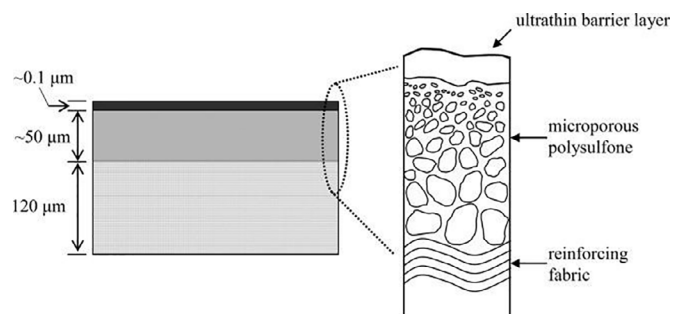
**Fig. 4**

Schematic diagram of two types of fouling in porous membranes: external fouling and internal fouling. Adapted with permission from Ref. [46].

refers to a surface modification, such as surface grafting and surface coating; 3D modification, including surface segregation and physical blending of polymers or polymeric matrices and organic/inorganic fillers [47]. For example, UF membranes made from PVDF/CA blends possessed improved hydrophilicity over the neat membranes [52]. An increasing CA proportion in the membrane leads to a significant enhancement of water flux (pure water flux increasing from 315 L/m²h to 522 L/m²h, with corresponding CA content from 10% to 20%) and antifouling property, which derives from the enhanced porosity and hydrophilicity as well as pore size increase by the introduction of CA. Polyvinyl chloride (PVC) was blended with polyvinyl formal (PVF) to fabricate UF membranes with stable antifouling properties [53]. Robust PVF tended to accumulate to membrane surface via surface segregation, which greatly improve the membrane surface hydrophilicity. Antifouling property endowed by fillers has been summarized [54]. From the perspective of membrane components, we consider coating and grafting on the membrane surface as the top protective layer and discuss this topic in a later section. Overall, 2D modification has a drawback of the sacrifice of permeability and can be applied as a post-treatment method, while 3D modification can only be used to construct new membranes [47]. The current antifouling strategies have been developed with a deeper understanding of fouling mechanisms and the relationships between membrane structures and performances, which is also required for future membrane designs. Many reported antifouling membranes have been tested with a specific type of foulant in laboratory conditions. More efforts should be encouraged to be made on developing and testing antifouling membranes in real application conditions.

3.2 Thin-film composite (TFC) membranes

Thin-film composite (TFC) membranes have experienced rapid development since Morgan first proposed to apply interfacial

**Fig. 5**

Schematic diagram of a typical thin-film composite membrane. Adapted with permission from Ref. [9]. Copyright © 2010 Wiley Periodicals, Inc.

polymerization (IP) for forming a thin polymeric layer onto a substrate in 1965 [55,56]. TFC membranes, proven to be both efficient and cost-effective [57], currently dominate the global market of NF, RO and FO applications [18,58]. Typical TFC membranes consist of three layers: (i) the top barrier layer (also called (polyamide) active layer, selective layer, or separation layer) is an ultrathin dense layer made by interfacial polymerization usually from polyamide; (ii) a microporous support serving as the middle layer, usually made from PSF; the bottom layer is often a commercially available nonwoven fabric substrate made from polyethylene terephthalate (PET/polyester), which provides additional mechanical strength [9,59] (Fig. 5).

TFC membranes exhibit excellent water permeability and salt rejection (nearly 100% NaCl removal) [60] with stability over a wide pH range of 2–11 [14]. For TFC membranes, the properties of each layer can be individually designed and optimized. Accordingly, their manufacturing cost is higher than that of conventional asymmetric cellulose-based RO membranes, because at least two preparation steps have been required. The drawbacks of polyamide TFC membranes are their poor chlorine tolerance [61], chemical resistance and fouling issue. Water disinfection is necessary for getting drinking quality water, while chlorine is the most common and cost-effective disinfectant. Therefore, developing chlorine tolerant TFC membranes are of vital importance for drinking water purification.

Non-porous, highly crosslinked aromatic polyamide (PA) usually serves as the top selective layer by interfacial polymerization, which occurs at the interface between two immiscible monomers/solvents [62]. Commonly, *m*-phenylene diamine (MPD) and trimesoyl chloride (TMC) are the two main active monomers for the PA layer formation for the RO process, while piperazine (PIP) and TMC are used for NF membranes [4,63]. Different derivatives of amines and acyl chloride have been developed for TFC membranes with different properties [56]. The properties of monomers, including solubility, diffusivity, functional groups, and the composition of monomers (and/or additives) impacting the roughness, hydrophilicity, and thickness of the thin film, further determine the filtration performance. Monomers developed in recent years and their applications were summarized in several recent reviews [11,60,64].

Moreover, the control of thickness, roughness and chemical composition of the PA selective layer is critical for the membrane

performance [65]. The reduction of active layer thickness is crucial for high water permeability and a small system footprint for industrial applications [66]. Many strategies have been proposed to optimize the structure and/or morphology of the selective layer, as well as novel/modified IP techniques [66]. For example, a molecular layer-by-layer (mLbL) assembly strategy could be used to control the selective layer roughness and thickness precisely, which was independent of specific polyamide chemistry, and allowed high water flux and NaCl rejection ratio of 98.2% [65]. A systematical study of the relationship between polyamide separation layer morphology and the filtration performance, particularly water flux, was reported by Xu et al. (Fig. 6a) [67]. They proposed a three-stage formation mechanism of the polyamide layer and found that the pores on the back surface of the polyamide separation layer were required to achieve high water flux, because these pores connecting with single-layer voids inside the PA layer, could function as water passages on the interface between the PA selective layer and the support layer. It was also shown that the creation of nano-sized voids demonstrated tunability on membrane roughness and enhancement in water permeability, salt rejection and antifouling property [68,69]. By introducing an increasing dosage of NaHCO_3 into the amine solution, Ma et al. prepared a series of TFC membranes with nano-foamed PA layers having an enhanced water permeability and a better NaCl rejection, as shown in Fig. 6b–c [69]. The TFC membrane with belt-crater morphology (TFC-6 in Fig. 6c) demonstrated the best performance.

Fouling, especially biofouling, like bacteria being generated during the filtration process, deteriorates the flux and salt rejection of TFC membranes. A large number of publications reported various strategies to enhance the antifouling properties of the PA layer. The strategies include chemical approaches, such as designs of new monomers and composition, application of random copolymers; physical approaches, such as the incorporation of organic/inorganic additives (e.g., $\text{Ca}(\text{HCO}_3)_2$ [70], NaHCO_3 [69], capsaicin derivative [71]), and various surface modifications [72,73].

Many studies aimed to address the problem of chlorine attack and subsequent oxidative degradation of PA TFC membranes, which is caused by two possible failure mechanisms, i.e., conformational changes and cleavages of the polymer chain [74]. A secondary interfacial polymerization approach was developed to alleviate the interaction between free chlorine and unreacted amino groups [75]. Protective coating and grafting [76], incorporation of nanoparticles (e.g., cellulose nanofibers [77]), and functionalized monomers, are also the topics of recent studies to prepare chlorine-resistant TFC membranes. Several recent reviews have provided detailed descriptions of these challenges [78,79]. Whilst, most of these strategies are limited in the laboratory and cannot yet be applied to large-scale fabrication methods for commercialization, and most of the novel membranes are estimated in short terms with highly idealized feed solutions, which usually considers only limiting factors [79]. A cost-effective fabrication process for TFC membranes with antifouling property, chlorine resistance, long-term stability, and health harmlessness for water purification remains a challenge, worthy of further consideration.

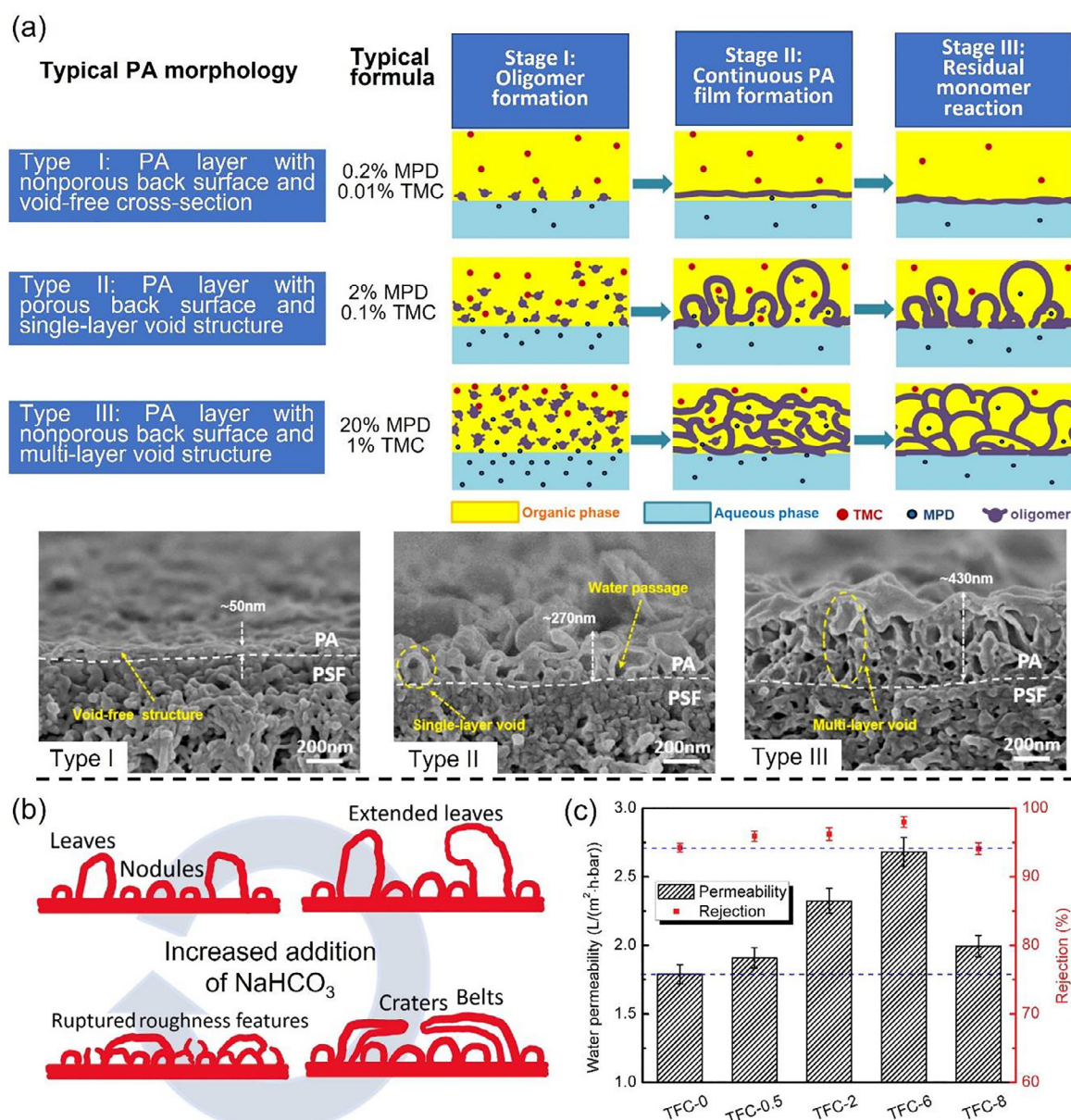


Fig. 6

(a) Schematic representation of the formation mechanism of polyamide separation layer and SEM images of the three types of PA layers, and (b) Schematic diagram of nano-foamed polyamide layer and the water permeability and NaCl rejection of the TFC membranes (TFC-n, where n represents of NaHCO_3 loading (0, 0.5, 2, 6, 8 wt%)). Adapted with permission from Refs. [67] and [69]. Copyright © 2017 Elsevier B.V and © 2019 Elsevier Inc. All rights reserved.

Even with the wide usage of polyamide TFC membranes in the RO and NF processes, these membranes are still at the mercy of the permeability-selectivity trade-off. Because of the fast kinetics of interfacial polymerization and the diffusion of amine monomers [80], precise control of the PA layer is hard to achieve while adding an interlayer between the PA selective layer and the support layer is promising to break the trade-off (shown in Fig. 7a–c) [81]. Organic interlayers are mainly constructed by polydopamine [82,83], tannic acid [84,85], and some other organics. A membrane with a PVA interlayer reported by Zhu et al. showed potential for practical water purification (Fig. 7d–f) [86]. The membrane consisting of a

polyamide selective layer with a thickness of 9.6 nm and a PVA interlayered PES substrate had been tested in both lab and pilot scale, exhibiting favorable water permeance of $\sim 30 \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$ and Na_2SO_4 rejection of $\sim 99\%$ [86]. A variety of nanomaterials, such as carbon nanotubes [87], graphene oxide (GO) [88], covalent organic framework [89], metal-organic framework [90], as well as nanocomposite (at least one of the two components is nanomaterial) [91], have been developed as interlayer materials. A recent investigation showed, after the introduction of interlayer into a TFC membrane, the median polyamide layer thickness was 25 nm, which was much thinner than 79 nm of conventional TFC membranes, contributing to the increase of water permeability

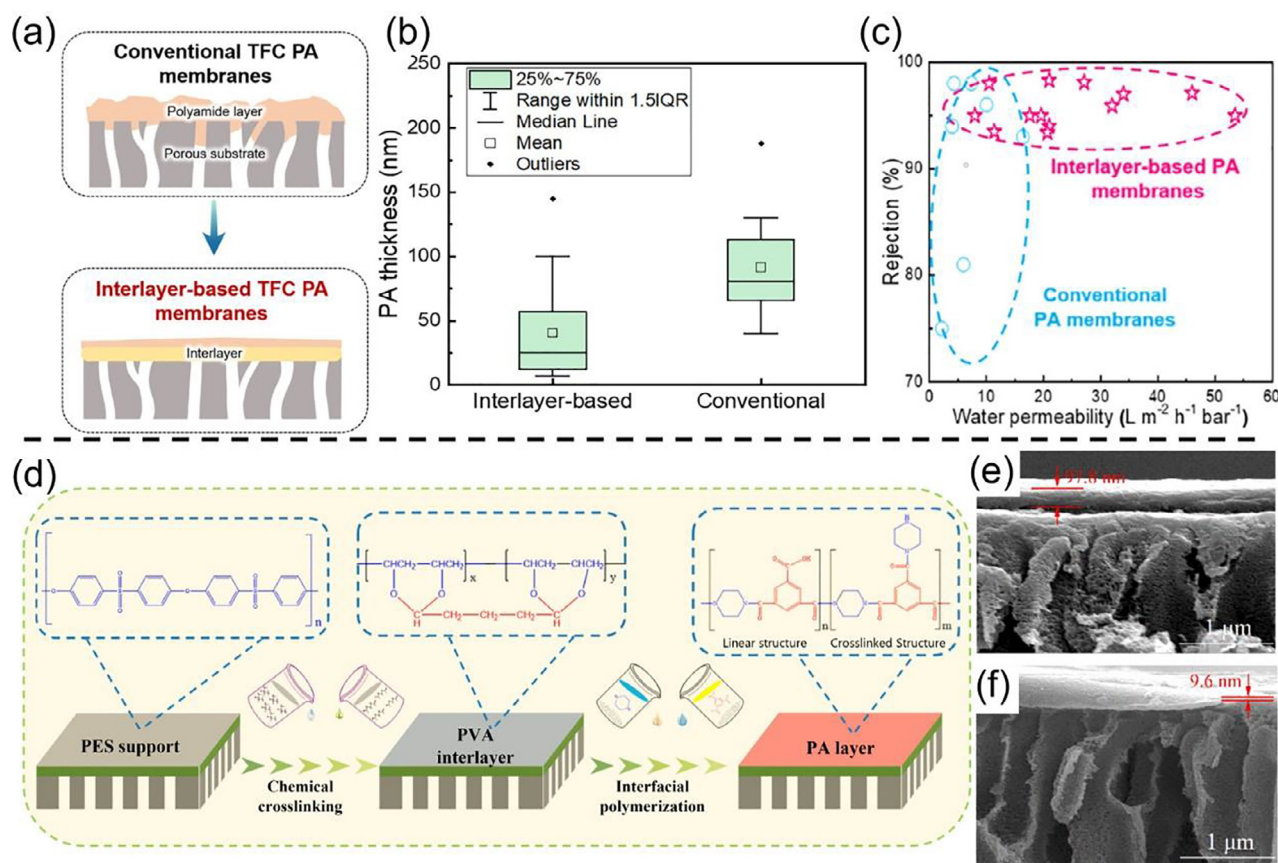


Fig. 7

(a) Schematic diagram of conventional TFC PA membranes and interlayer-based TFC PA membranes; (b, c) Thickness and nanofiltration performance of conventional and interlayer-based TFC PA membrane based on an investigation; (d-f) Schematic diagram of the preparation process of a TFC membrane with PVA interlayer, and cross-section SEM images of a conventional TFC membrane (e) and the PVA-interlayered TFC membrane (f), respectively. Adapted with permission from Refs. [81] and [86]. Copyright © 2020 Elsevier B.V. All rights reserved. Copyright © 2020, American Chemical Society.

of TFC membranes. Simultaneously, the interlayer-based TFC membranes exhibited enhanced/maintained Na_2SO_4 rejection better than in conventional membranes (Fig. 7b, c) [81]. Detailed discussions for mechanisms and materials could be found in several recent reviews [81,91–93]. Organic continuous interlayers usually have tight adhesion with substrates, and those with porous and hydrophilic properties could also enable firm intrusion of the PA layer. Among various interlayers, TFC membranes with organic interlayers have the most potential for commercial scale-up. However, the scalability of current methods for interlayer fabrication is still limited [81].

3.3 Electrospun nanofibrous membranes

The rapid development of nanotechnology had greatly freshened up the filtration membranes for various applications. Electrospun nanofibrous membranes (also called ENMs [94]) with excellent performance, low environmental impact and low energy consumption are considered ideal candidates for future water purification membranes [19,95]. Among different techniques to produce nanofiber scaffolds [96,97], the electrospinning technique, introduced by Reneker's group in 1993, has evolved toward large-scale operations.

Compared with the porosity of commercially available membranes (usually 60–80 vol%) [98], electrospun nanofiber scaffold always possesses much higher porosity (usually > 80 vol%, up to 95 vol%) [99,100]. The pore size can be controlled directly by varying the fiber diameter [101]. A typical advantage of nanofiber scaffold is the large surface area, allowing abundant functional adsorption sites, and thus permitting high retention of contaminants by depth filtration or adsorption [102,103]. Except for traditional close-void pores, nanofiber scaffolds with interconnected pores have been developed for high permeation flux, low hydraulic resistance with fewer fouling propensities [104]. The deformation under high pressure is the major drawback of these scaffold membranes. It could be improved by adjusting of electrospinning parameters and the introduction of additives. All these properties allow the nanofibrous scaffold to quickly emerge as membranes for MF/absorption applications, ultrafiltration, and membrane distillation (MD), and also as the support layer for NF, RO and FO membranes. The electrospun nanofibrous membranes have been constructed into one-, two-, three-, and four-layered structures for different demands of membrane properties [105].

Multiple reviews have provided summaries from various perspectives on electrospun nanofibrous membranes, including

preparation, characterization, and applications Feng et al. [106]. The relative characterizations [107], electrospun nanofibrous membranes as the barrier layer with emphasis on reinforcement and post-treatment [108], reviews of electrospun nanofibrous membranes for mass production with emphasis on water purification [19], and non-woven electrospun water purification membranes with typical polymers [109] are available. Functionalized electrospun nanofiber membranes were also reviewed recently by Chen et al. [110]. Another recent review summarized the applications of electrospun nanofibers in pressure-driven water treatment [111]. Electrospun nanofibrous membranes for desalination have also been reviewed [94,112]. Recent attention tends to improve the membrane structures layer by layer. Here, in terms of membrane components, some examples of barrier layers made from polymeric electrospun nanofibers for different applications are presented as follows.

3.3.1 Microfiltration

Electrospun nanofiber scaffolds with low basis weight, high porosity and pore sizes ranging from 0.1 to 10 μm , are suitable as barrier layers for both filtration and adsorption processes [105]. Some drinking water sources, like surface water, contain natural organic matter, microbial pathogens, as well as surfactants and toxic metals if the source is contaminated by wastewater [14]. Then, to obtain clean and safe drinking water, electrospun scaffolds can be utilized for removing micron- or submicron-size contaminants, and also adsorbing metal ions and organic compounds. The adsorption applications were summarized in recent reviews [113,114]. Membranes made from electrospun nanofibers for MF can have either a one-layered structure, that is a self-supporting membrane, or a multi-layered composite at least consisting of an electrospun nanofiber scaffold as the effective layer for separation and a nonwoven substrate (e.g., PET substrate).

Self-supporting membranes fabricated from PVDF and PSU nanofibers can be used to remove micron-size impurities in water, whilst the rejection ratio is sometimes limited [115,116]. Bazargan et al. prepared a self-supporting electrospun PAN nanofibrous membrane with high permeability, high dirt-loading capacity and low-pressure drop, which enabled by the consistent and defect-free membrane structures by controlling the electrospinning process [117]. Recently, self-supporting (free-standing) nanofibrous composite membranes were fabricated with thin PAN nanofibers as the functional scaffold and thicker PVA nanofibers as the skeleton scaffold [118]. The membrane properties could be controlled by factors, such as polymer concentration. The sufficient mechanical strength and high-water permeability were achieved by the interpenetration of the two components as shown in Fig. 8a [118]. These composite membranes were applied as MF filters with an adsorption capacity of 133 mg/(g PAN nanofibers) against Cr (VI) ions, exceeding those of commercial adsorbents [118]. Further modification of PAN has led to improved separation efficiency and selectivity for particular sized-microspheres with positively or negatively charged nature for excellent adsorption capability [119].

Multi-layered nanofibrous MF membranes can demonstrate a combination of properties from the components. A membrane with a mean pore size of $0.22 \pm 0.01 \mu\text{m}$ and a maximum pore size of $0.62 \pm 0.03 \mu\text{m}$, was fabricated from electrospun PAN nanofibers on PET nonwoven substrate by the Chu and Hsiao group. The membrane exhibited a high flux and a high rejection of 99.99% of bacteria, exceeding commercial MF membranes possessing the same mean pore size [120]. These nanofibrous MF membranes could be further modified: the infusion of nano-absorbents, such as ultra-fine cellulose nanofibers [121,122] and cellulose nanowhiskers [123], into the nanofibrous barrier layer; the introduction of bi-vinyl and tri-vinyl monomers by *in situ* polymerization has further enabled the adsorption functionality [124]. For example, with

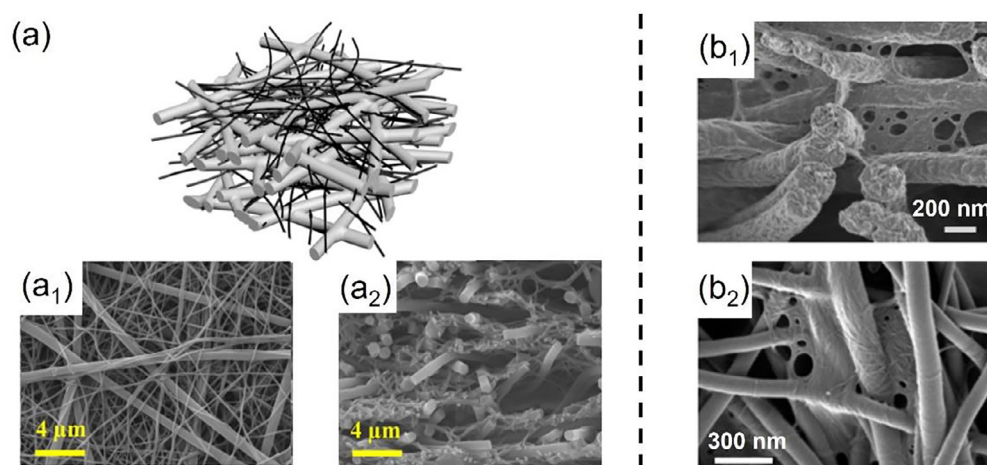


Fig. 8

(a) Schematic representation of an interpenetrating nanofibrous composite membrane consisting of thicker PVA nanofibers as the skeleton scaffold and thinner PAN nanofibers as the functional scaffold, and top view (a_1) and cross-section (a_2) SEM images of an interpenetrating nanofibrous composite membrane (glutaraldehyde-crosslinked PVA12%/PAN10%); (b_1 , b_2) SEM images of nanostructures of PAN nanofibrous barrier layer infused by m-UFCNs (b_1) and MCCNs (b_2), respectively. Adapted with permission from Refs. [118] and [122]. Copyright © 2019, American Chemical Society and © 2011, Oxford University Press.

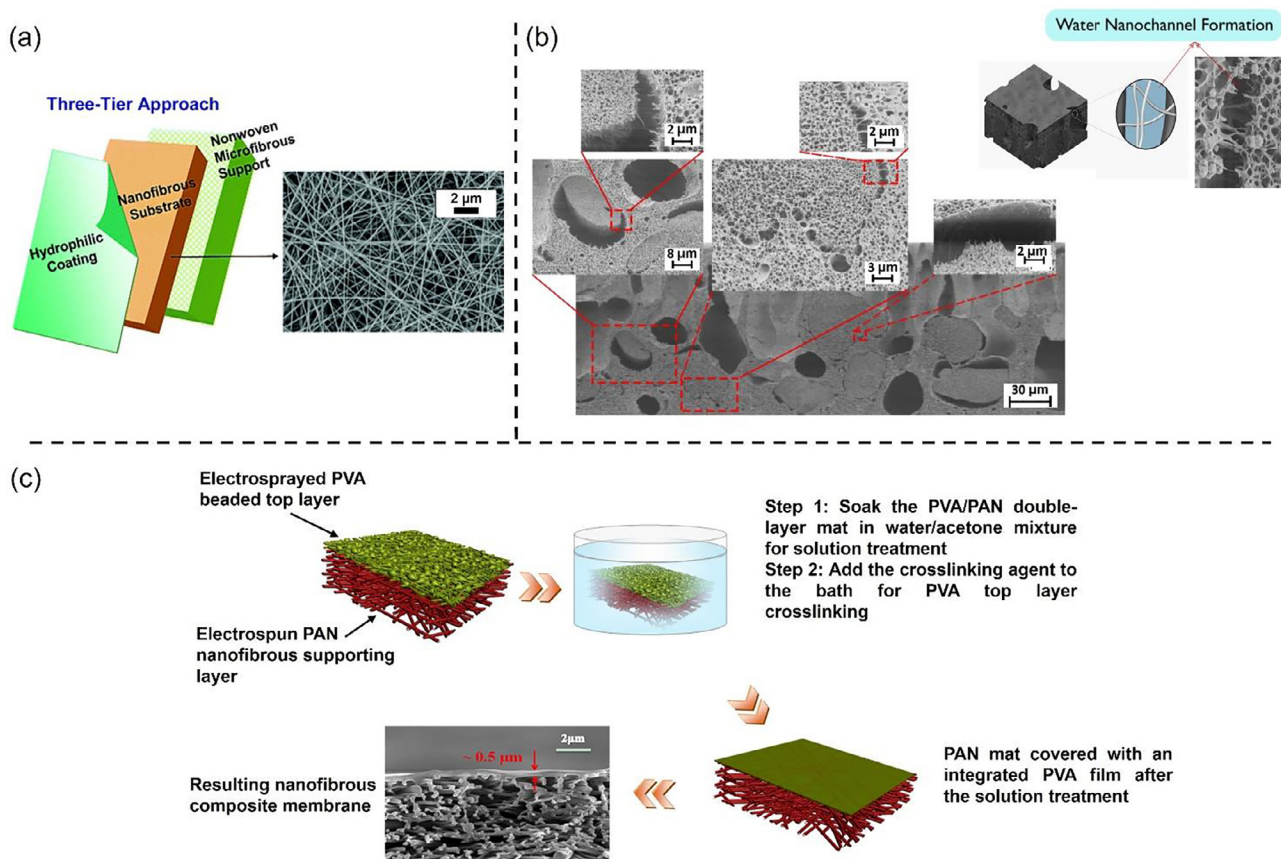


Fig. 9

(a) Schematic illustration of the three-layer TFNC membrane; (b) Cross-section SEM images of a cellulose nanofiber (CNF) embedded cellulose acetate nanocomposite membrane, and schematic diagram of water nanochannels inside the nanocomposite membrane; (c) Schematic diagram of the preparation procedure of a TNFC membrane with electrospinning technique combined with solution treatment. Adapted with permission from Refs. [125,134,129]. Copyright © 2005, American Chemical Society and Copyright © 2012 Elsevier B.V. All rights reserved.

the incorporation of modified ultra-fine cellulose nanofibers (m-UFCNs) and microcrystalline cellulose nanofibers (MCCNs) into a PAN nanofibrous scaffold on PET substrate, different nanostructured barrier layers could be generated. The m-UFCNs network entangled with the PAN microfibers, forming a quasi-three-dimensional structure (Fig. 8b₁), while MCCNs wrapped around the microfibers locally (Fig. 8b₂) [122].

The versatile electrospinning technique with a deeper understanding of operations and solution parameters in recent years has endowed electrospun nanofibrous membranes with a good control of the pore structures. These nanofibrous membranes could be further modified and enhanced in more flexible and convenient approaches, compared with the modification of conventional MF membranes which often face the challenge of compatibility. With excellent performance as barrier layers for both filtration and absorption purposes, electrospun nanofibrous membranes have become desirable candidates to replace the conventional MF membranes.

3.3.2 Ultrafiltration

The natural water source of drinking water can be contaminated by pollutants, such as emulsified oils and surfactants from produced water. When dealing with oil

emulsions with sizes less than 50 nm, nanofibrous MF membranes usually with pore sizes larger than 100 nm are not sufficient to separate these oily impurities. Fortunately, ultrafiltration operated by a thin-film nanofibrous composite (TFNC) membrane is a cost-effective approach for effective oil/water separation to get clean drinking water, which has been reviewed previously [19,105]. In the TFNC membrane systems, the electrospun nanofiber scaffolds could not only serve as barrier layers, but also play an important role as support layers. Here, we discuss these two functions of TFNC UF membranes together for convenience.

The first TFNC membrane for the removal of oil emulsion in water was reported by Wang et al., which consisted of a nonporous hydrophilic coating layer, an electrospun PVA nanofibers midlayer, and a traditional nonwoven fibrous substrate, as shown in Fig. 9a [125]. In the past decade, crosslinked PVA coating/hydrogel [100,126,127], PVA nanofibers [128], PVA nanobeads [129,130], ultrafine polysaccharide nanofibers [131,132], and ultrafine cellulose nanofibers [121,133] have been developed as the top barrier layer in the TFNC membrane system. In addition, a variety of approaches was developed to mitigate the penetration of the casting solution into the nanofibers substrate and thus to optimize the barrier layer thickness [19]. For instance, a TFNC membrane containing a top barrier layer made from

ultrafine polysaccharide nanofibers, i.e., cellulose and chitin, with diameters of 5–10 nm, a midlayer made from electrospun PAN nanofibrous scaffold and a PET nonwoven support, demonstrated ten times higher permeation flux and a high rejection ratio over commercial UF membranes for oil/water separation [132].

The incorporation of nanofillers into polymeric membrane matrix could lead to the interconnection formation of water nanochannels in the membrane structure, which has been found to further improve the separation performance [105]. For example, Fig. 9b shows that the introduction of cellulose nanofibers into the cellulose acetate membrane matrix caused the formation of water nanochannels [134]. These interconnections enabled water molecules to pass through the membrane easily, resulting in a highly increased flux of 102 L/m²h with a slightly decreased Bovine Serum Albumin (BSA) selectivity. Similarly, a nanofibrous composite UF membrane, with an interpenetrating cellulose nanofiber-polymer network containing negatively charged water channels in the barrier layer, exhibited a high water transportation rate of 147.1 L/m²h and a high rejection ratio of 98.4% against charged BSA [135].

Various types of fabrication and modification techniques and strategies have been developed including functionalization of nanofibers, layer-by-layer method, surface adhesion by electrospaying technique, solution blending process and wet chemical treatment technique, etc. [136]. For example, a PVA/PAN TFNC membrane was prepared by electrospaying PVA on an electrospun PAN nanofibrous support followed by a solution treatment, exhibiting a high flux of 347.8 L/m²h and a high rejection ratio of 99.6% under an operating pressure of 0.2 MPa (Fig. 9c) [129]. Similarly, a facile route for fabricating TFNC membrane consisting of a hydrophilic barrier layer and a nanofibrous substrate, was fabricated by electrospaying PVA nanobeads onto an electrospun PAN substrate [130]. The chemically cross-linked barrier layer demonstrated controllable filtration performance by tuning PVA crosslinking degrees. It exhibited high UF performance against BSA with a permeation flux of 173.0 L/m²h and a rejection ratio above 98% at a low feeding pressure of 0.3 MPa [130]. Tian et al. recently demonstrated a TFNC membrane to separate oil-in-water emulsions with self-cleaning and antifouling properties and achieved by spraying and crosslinking ultrathin carbon nanotubes onto an electrospun nanofibrous PAN substrate [137]. The resultant membrane exhibited a flux of 60 L/m²h and a rejection ratio of 95% under a very low pressure of 20 kPa.

The three-layered TFNC membranes have demonstrated significantly better UF performance than conventional UF membranes, such as the high permeation flux and the low fouling tendency. The high permeation flux could be further improved through the water nanochannels by incorporating nanofillers into the barrier layers. In addition, some integration between the barrier layer and the electrospun nanofibrous support could increase the mechanical stability of the barrier layer and also introduce water channels to benefit water transportation [105]. Therefore, TFNC membranes are cost-effective and promising candidates for future UF applications in practical cases.

With many strategies, such as the introduction of additives, surface coating, and bionic design (e.g., lotus leaf-like bionic

membrane [21]), the electrospun nanofibrous membranes can be developed into superhydrophilic membranes for water removal, superhydrophobic membranes for oil removal and intelligent membranes with switchable wettability for the removal of water or oil [22,138]. Generally, these membranes are used in industrial oily wastewater treatment.

3.3.3 Membrane distillation (MD)

Membrane distillation (MD) is used for extracting fresh water from various saline sources. It is a thermally driven separation process, which is based on vapor-liquid equilibrium, and needs a supplied heat source [139]. The hydrophobic membrane allows the passing of water vapor that will then condense and coalesce into liquid droplets, while the liquid feed cannot. Compared with RO and FO, the MD process has advantages including low operating pressure, small system footprint, concentration-independent operation, and flexible sources of the driving force [112]. To operate the MD process, the membranes are supposed to have a highly porous structure with a small average pore size ($< 0.2 \mu\text{m}$) [104], high hydrophobicity, and low scaling tendencies [140]. Current commercial MD membranes have commonly used conventional MF and UF membranes made from PVDF, PTFE, PE, PP via processes including phase inversion, thermally induced phase separation, sintering or stretching [141]. However, the efficiency of these membranes has been limited due to low hydrophobicity, low permeability, as well as wetting and fouling tendency. Exhibiting high porosity, interconnected pores, adjustable pore size, and high surface-volume ratio, electrospun nanofibrous membranes are ideally suited for enhanced MD operations.

Many hydrophobic polymers, such as PS, PVDF, PVDF-HFP [142], fluorinated polytriazole (FPTA) [143], and styrene-butadiene-styrene (SBS) [144], have been used to prepare electrospun nanofibrous MD membranes. Strategies aimed to improve properties like anti-wetting capability and mechanical stability, access through either conducting modification on nanofibers or macroscale treatment to the membrane [145,146]. The functionalization via incorporation of hydrophobic nanomaterials, such as polyhedral oligomeric silsesquioxane (POSS) [147], TiO₂ [148], multi-walled carbon nanotubes [149], MOFs [150], polymer nanoparticles [151], has been shown to amplify membrane performance efficiently. To address the typical obstacle of MD membranes, e.g., the wetting caused by matters with low surface tension, various surface treatments have been used to introduce superhydrophobicity [146,152]. Inspired by nature, the morphologies of nanofibers could be modified into lotus leaf-like, pine needle-like surfaces with high roughness and superhydrophobicity, mitigating membrane wetting and fouling [20,153,154].

Typically, pristine electrospun nanofibrous MD membranes could be made into a one-layer structure with both features for MD applications and sufficient mechanical strength [151,154,155], or be fabricated by electrospinning functionalized polymer solution onto the support, which could be a commercially available fibrous substrate [150,156], or an electrospun nanofibrous support layer with specific properties [157].

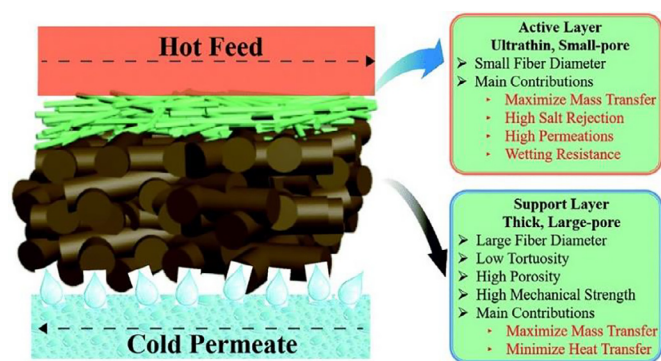


Fig. 10

Schematic illustration of a hierarchical MD membrane with a thin active layer made from thinner PH nanofibers and a thick support layer made from thicker PET microfibers. Adapted with permission from Ref. [162]. Copyright © 2019, Royal Society of Chemistry.

The intrinsic trade-off between heat and mass transfer confines the achievement of a high-performance and cost-effective MD membrane process: a thin membrane always leads to high permeation but high thermal loss simultaneously. The asymmetric membrane has been shown to be a solution to break this trade-off limitation by both increasing the thickness of the support layer to mitigate heat transfer and decreasing the thickness of the hydrophobic layer to diminish mass transfer resistance. Commonly, the polymeric support layer possesses low conductivity with high porosity. Applying composite membranes to MD was proposed first by Cheng and Wiersma [158]. Since then, dual-layer hydrophobic/hydrophilic flat sheets have been studied as MD membranes due to their high performance over conventional single-layer hydrophobic membranes. Qtaishat et al. did systematic studies on dual-layer MD membranes and explored the effect of layer thickness on performance [159–161]. Typically, dual-layer MD membranes consist of a hydrophobic layer on the feed side, onto a support layer on the permeate side which can be either hydrophobic or hydrophilic (such as PH/PET membrane [162], PVDF-silica/PVDF membrane [163], aPP/PVDF membrane [164], and styrene-acrylonitrile (SAN)/PAN membrane [165]). For example, a dual-layer composite membrane consisting of a thin dense layer made from small poly (vinylidene fluoride-co-hexafluoropropylene) (PH) nanofibers and a thick support layer with large PET microfibers, is shown in Fig. 10 [162]. The thin PH layer allows high mass transfer, while the thick PET substrate restricts heat transfer. With the optimized thickness of PH active layer and PET support layer of 3 and 70 μm , respectively, this membrane could achieve an extremely high water flux of $79.21 \pm 4.17 \text{ L/m}^2\text{h}$ and a salt rejection above 99.9% with 3.5 wt% NaCl solution as the hot feed in direct contact membrane distillation [162].

Furthermore, triple-layered composite membranes have also been reported for MD applications. Prince et al. prepared a long-term stable triple-layer MD membrane, consisting of a thin hydrophobic nanofibrous PVDF selective layer, with a conventional microporous PVDF middle layer and an additional PET support layer. The membrane demonstrated higher water

flux, lower salt penetration and better long-time stability than conventional dual-layer MD membranes [166]. An introduction of an intermediate hydrophilic layer between two hydrophobic layers to form a triple layer membrane, was also studied but showed reduced direct contact membrane distillation performance due to the formation of water pockets [167]. Recently, Ali et al. proposed a triple-layer MD membrane by electrospaying PS microbeads on a dual-layer SAN/PAN membrane, reaching enhanced surface hydrophobicity and increasing permeate flux from $67.52 \text{ kg/m}^2\text{h}$ to $84.4 \text{ kg/m}^2\text{h}$, exceeding the performance of commercial PTFE membrane [165].

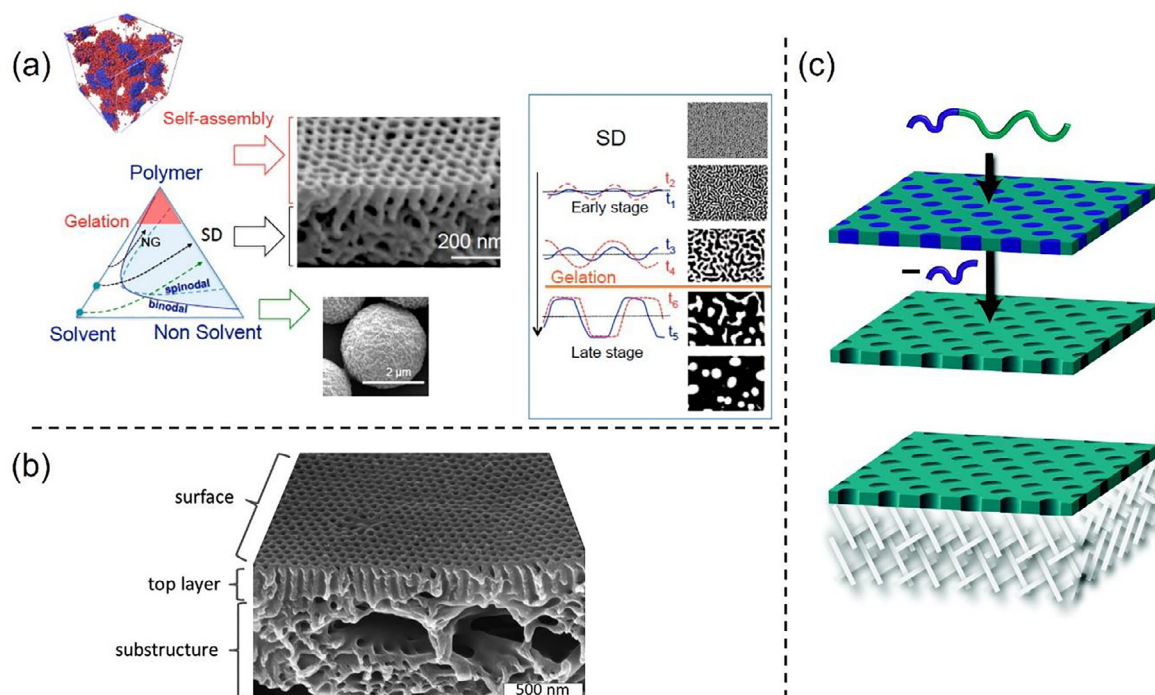
3.4 Block copolymer membranes

Block copolymer (BCP) membranes have experienced rapid development in recent decades, since the first report of BCP membranes by Lyman et al. in 1963 for blood dialysis [168,169]. Compared with homopolymers, block copolymers have been used much less to fabricate water purification membranes. BCP membranes possess narrow pore size distributions, excellent pore size tunability, and a flexible functionalization capacity, making them desirable for future water filtration applications [170]. Other advantages of BCP membranes include flexible control of permeability, thickness, fluidity, and thermal, chemical, and mechanical stability as well as a longer lifetime [171].

It has been well established that BCP can separate into a series of structures, such as cubic, cylindrical, bicontinuous cubic, lamellar and the corresponding reverse phases. Among these self-assembled structures, hexagonally packed cylindrical structures and bicontinuous cubic structures have been utilized for filtration membranes [14]. The cylindrical structures usually work with the cylindrical pores aligned perpendicularly and continue to the film surface, while bicontinuous cubic structures can offer interconnected pores all over the membrane with accordingly higher hydraulic resistance.

Generally, self-assembly and nonsolvent-induced phase separation (SNIPS), and selective block removal are the two dominating strategies for pore generation [172]. The fast one-step SNIPS technique developed in 2007 [173], is considered a very promising technology for scalable and facile fabrication processes today. The membranes fabricated by the SNIPS approach consists of three continuous layers: (i) disordered spongy substrate in the bottom ($> 20 \mu\text{m}$), with the shaping process being guided by spinodal decomposition (SD), having a larger pore size and a wider size distribution; (ii) an ordered assembled layer in the middle (up to 400 nm), having vertically aligned cylindrical pores with a narrow pore size distribution; and (iii) a very thin top surface layer ($< 100 \text{ nm}$) [172]. The three-layer membrane structure is shown in Fig. 11a, b [172,174]. The other approach with selective block removal yields a thin cylindrical film via a two-step process that the block copolymers self-assemble firstly and then follow a subsequent selective etching or partial dissolution of the minority domains (Fig. 11c) [170]. The separation layer prepared by this process requires it to be on top of a macroporous support layer, e.g., a PVDF substrate [175].

Most accessible BCP membranes have pore sizes in the range of 5–50 nm, which belong to ultrafiltration [14]. Recent progress has expanded their applications from UF to NF and RO processes,

**Fig. 11**

(a) Combination of self-assembly and nonsolvent-induced phase separation mechanisms in the formation of isoporous flat-sheet membranes (casting solution in the semidiluted concentration regime) and porous particles (less concentrated starting solution); (b) Representative SEM images: top view and cross-section of a PS-*b*-P2VP block copolymer membrane; (c) Schematic representation of the formation of a cylinder-forming diblock copolymer membrane by selective block removal method. Adapted with permission from Refs. [172,174,170]. Copyright © 2016, American Chemical Society, Copyright © 2015 Wiley Periodicals, Inc., Copyright © 2010, American Chemical Society.

via various strategies, such as BCP molecular design [176] and post-modification [177,178]. For example, an asymmetric PS-*b*-PEO membrane demonstrated a high and stable pure water flux of about 800 L/m²h, a rejection ratio of 67% against BSA and 99% against γ -globulin as well as good mechanical stability [179]. Some recent reviews have provided detailed descriptions about the structure formation mechanism, design strategies (such as pore size control, functionalization), properties evaluation and modules (flat sheets and hollow fibers) [170–172,174,180]. Although most strategies for BCP membrane improvement are in the laboratory stage, the SNIPS process remains promising for scaling up the manufacture due to its relatively low technology requirements. The current industrial installation to produce commercial porous membranes can be used for the SNIPS process. Therefore, the BCP membranes could be produced at low costs if the applicable block copolymers are available [172].

4 Support layer

It is a general understanding that the main filtration performance is determined by the selective layer (i.e., the PA selective layer in TFC membranes), while the support layer mainly provides mechanical support. Recent studies have shown the negligible influence of the support layer on the PA selective layer formation and ultimate performance [4–8]. Conventional MF and UF membranes are usually topped on a commercially available non-woven fibrous substrate. For TFC membranes being used in NF, RO and FO processes, except for the non-

woven substrate at the bottom of the membrane, the support layer beneath the PA selective layer (also called sublayer or substrate), can be tailored to the needs of specific properties. On the one hand, the support layer properties determined the performance of the support layer itself, such as pore features, mechanical strength and antifouling capacity. On the other hand, the support layer was proven to affect the PA layer formation, i.e., the interfacial polymerization reaction, thus impacting the membrane morphology and structures as well as the ultimate separation performance. Several recent reviews have been discussed with different emphases [4–8,93].

4.1 Conventional support layers

Porous materials are commonly used as the substrate for the TFC membranes in pressure-driven processes (i.e. RO, NF) due to their contribution to water flux enhancement [181]. PSF and PES are the most widely used polymeric materials to prepare the support layer of TFC membranes for the RO process [182]. Other polymers could also be used as support layer materials, such as PAN, PTFE, polyimide, PP, PVDF, polyether polyurethane (PF), polyketone (PK), poly(arylene ether nitrile ketone) (PENK), polyetherimide (PEI), etc. [7]. Among various variables, such as molecular weight of polymer and solvent type [7], polymer concentration was concluded as the most crucial factor that impacts the structure of the support layer, due to its direct influence on pore formation, roughness and thickness [4]. For FO membranes, the support layer needs to be thin, highly porous, hydrophilic and has a

low tortuosity and excellent chemical, thermal and mechanical stability [183]. Modified polymers, such as sulfonated polymers [184,185], sulfonated polymer blends [186], PAN [187], and cellulose triacetate [188], have been developed as materials for the support layer of FO membranes.

Abundant research has been conducted to tailor the support layer structures and performances. These strategies could be divided into three types: (i) addition of polymer additives (i.e., polymer blend); (ii) introduction of nanomaterials for construction of nanocomposite membranes; (iii) surface modification. Polyvinylpyrrolidone (PVP) and polyether glycol (PEG) are the most widely used hydrophilic polymeric additives, and their function and resulting membrane performance have been discussed previously [4]. Other additives include hydrophilic polymers, such as PAN and polyaniline (PANI), and sulfonated polymers, such as sulfonated poly(ether ketone) (SPEEK) and sulfonated polysulfone (SPSF). In terms of nanofillers for mixed matrix membranes, the filler can be either solid or mesoporous, from various materials including inorganic oxide, metals, metal oxide, and hydrophilic nanotubes (e.g., carbon nanotubes, halloysite nanotubes, imogolite nanotubes) [7]. However, the introduction of nanofillers usually comes with issues of even distribution and alignment of fillers and the safety concern of water quality. As an effective approach to the tailored membrane surface, surface modification for RO and FO processes has different focused points. Both RO and FO membranes experience external concentration polarization at the surface of the active layer, while internal concentration polarization (ICP), which occurs within the support layer and causes a reduction in water flux of more than 80%, is exclusive to FO [189]. Therefore, for RO membranes, improved water flux and antifouling properties are essential, while ICP is usually considered critical for FO membranes besides water flux [4].

It was found that a polydopamine (PDA) coating on the support layer of the TFC membrane enabled an increase in water flux and a decrease in ICP, which has scalability for TFC membranes for all osmosis applications [190]. Here, the possible interlayer (i.e., gutter layer), introduced between the PA selective layer and a support layer, could also be considered as a surface modification being applied on the support layer [6,7].

Recent studies revealed that the surface features of the support layer had a direct impact on the polyamide selective layer thickness, topology, and uniformity in TFC membranes [191]. In order to understand the exact role that the support layer has played on the PA layer formation, different conceptual models have been proposed [183,191–194]. The volcano-like models explained the ridge-and-valley surface structure, and the effect of pore size and hydrophobicity on the roughness of the PA layer: larger pores are conducive to the convection of amine monomers, leading to a rougher surface; more hydrophobic support favors eruption of amine solution, resulting in a rougher surface and higher water permeance (Fig. 12) [8,193]. The support layer also affects the internal nanovoids of the PA layer, which could be interpreted by interfacial degassing/vaporization theory [69,194–197]. Several recent reviews have provided detailed discussion [5,6,8]. These fundamental understandings on the relationship between the polyamide layer formation and the support layer

properties are promising to become useful guidance for the future improvement and design of TFC membranes.

4.2 Electrospun nanofibrous support layers

Electrospun nanofiber scaffolds, with high porosity, interconnected pores and high surface-to-volume ratio, have been utilized as the support layer for TFC membranes. The TFC membranes, consisting of a nonwoven fibrous substrate, an electrospun nanofibrous support layer and a barrier layer made from either crosslinked polyamide or nanofibers, were termed thin-film nanofibrous composite (TFNC) format [19,112]. The application of electrospun nanofiber scaffold enables the support layer high water flux and increased permeability that far exceeds conventional TFC membranes. Whilst, due to very high porosity and relatively weak adhesion between nanofibers [99], electrospun nanofiber scaffolds can easily experience an irreversible deformation, thus making them more suitable for low-pressure filtration such as the FO process. Overall, for both low-pressure filtration processes and high-pressure operations where electrospun nanofibers only take up the minority volume in the membrane structure, TFNC membranes could bring significant energy-saving benefits [105]. The application of TFNC membranes in water purification has been discussed in some reviews and book chapters recently [4,10,19,105,112].

The electrospun nanofibrous scaffold was first being used as a support layer for NF TFNC membranes in 2008 [4,198]. The TFNC membrane with a PAN nanofibrous support layer demonstrated a much higher permeate flux over conventional TFC membranes and a comparable rejection rate. The influence of pore size of the electrospun nanofibrous support layer on the filtration efficiency of the TFNC membrane was investigated in the NF process [199]. It was found that smaller fiber size leads to smaller pore size, and thus increased salt rejection rate at the cost of flux. Diverse factors, including additives, relative humidity, distribution of fiber diameter and the adhesion, of TFNC membranes with support (mid-) layer made from PES nanofibrous scaffold for the NF process was investigated by Tang et al. [200]. The wettability of the support layer was also shown to be important in the formation of the flawless thin barrier layer [201]. Ionic liquids were applied as non-reactive additives in preparation of the PA barrier layer which topped on the PES nanofibrous scaffold support and showed the effect on manipulating the permeation flux and the salt rejection rate [202].

To support a thin barrier layer with a thickness below 100 nm and to form a uniform nanocomposite structure, a three-layered TFNC membrane containing a composite barrier layer formed by polyamide interfacial polymerization around an ultrafine cellulose nanofibrous layer was demonstrated in the NF process (Fig. 13) [112,203]. The different arrangement of aqueous and organic phases could result in different membrane structures. The membrane fabricated by interfacial polymerization with an aqueous phase above the organic phase exhibited smaller pores and better NF performance since the dense part of the barrier layer was formed on the top of the nanofibrous substrate. This three-layered TFNC membrane was further optimized for the RO process and exhibited a flux of 28.6 L/m²h at 0.7 MPa and a rejection ratio

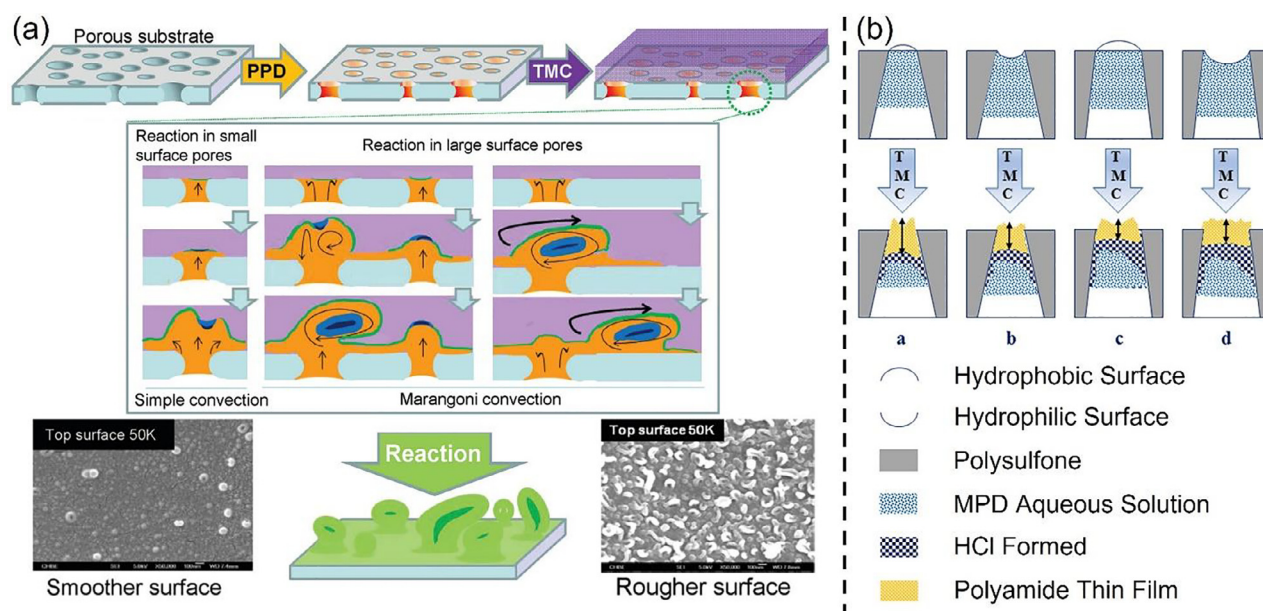


Fig. 12

(a) A conceptual model explaining how the pore size and distribution of support layer affect selective layer roughness, and (b) a conceptual model illustrating the role of polysulfone support membrane pore structure and chemistry during interfacial polymerization of polyamide thin film. Adapted with permission from Refs. [193] and [8]. Copyright © 2012, American Chemical Society and © 2021 Elsevier B.V. All rights reserved.

of 96.5% against NaCl, which is comparable to the performance of high flux commercial RO membranes [204].

The concept of directed water channels has been reviewed recently [112]. This concept has been applied to high-flux nanofibrous membranes by the Ma and Hsiao research team. As shown in Fig. 13 [112], the directed water channels could be incorporated in the barrier layer of the TFNC membrane through the integration of the polyamide matrix and the ultrafine cellulose nanofibrous layer, which demonstrated significantly enhanced flux and rejection [205]. The introduction of directed water channels in the barrier layer brings four advantages

over membranes without the water channels: firstly, these water channels are being generated by phase separation at the interface between any bicontinuous phases inside the barrier layer; secondly, the directed water channels have tunable sizes depending on the phase separation process, which enables flexible applications of the membranes; thirdly, the surface modification could endow the water channels with specific properties, such as hydrophobicity and charged surface; lastly, the controllable density of these directed water channels can enhance the mechanical strength of the membrane and maintain porosity simultaneously [205]. Recently a TFNC membrane containing

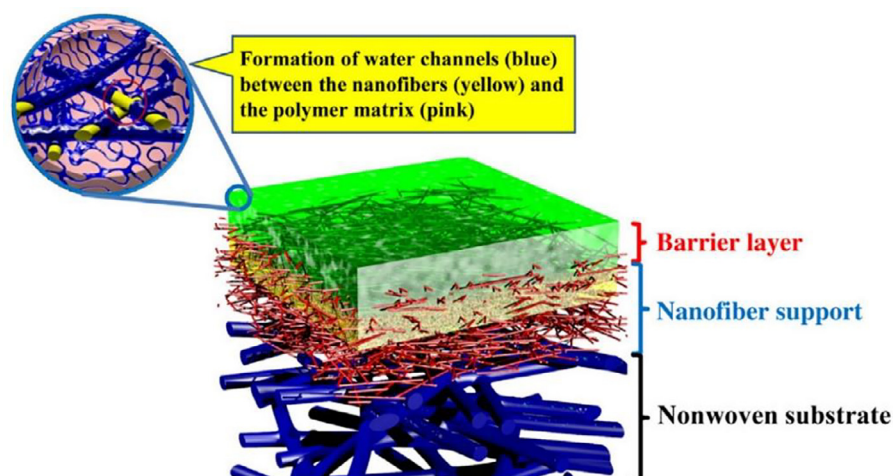


Fig. 13

Schematic representation of TFNC membranes with a polyamide barrier layer on CN/PAN/PET scaffold. Inside the barrier layer, directed water channels are formed by phase separation of electrospun nanofibers and polymer matrix. Adapted with permission from Ref. [112]. Copyright © 2019 Elsevier Inc. All rights reserved.

a tree-like electrospun nanofiber support layer was used for nanofiltration. The branches on PVDF nanofiber were generated by the splitting of polymer jets with the aid of an additive, tetrabutylammonium chloride, and subsequently embedded into the PA barrier matrix, leading to the formation of a high porosity support layer with directed water channels [206]. Membranes containing directed water channels are particularly desirable for NF, RO and FO processes, and could reach a higher water flux of 2–5 times when compared with similar membranes without water channels [10]. This membrane design shows the potential to be applied widely for enhanced membrane performance.

Many technologies have been developed for improving TFNC membrane properties. For instance, hot pressing of the electrospun nanofibrous scaffold before interfacial polymerization could tune the pore size and thickness of the nanofibrous support layer because of its cost-effectiveness without additional need for additives [4,207]. However, hot pressing enhances the adhesion between nanofibers at the expense of densification of interconnected structures of the nanofibrous scaffold, which would decrease water flux. Layer-by-layer assembly was also developed to modify the electrospun nanofibrous support for TFNC membranes [208,209].

Membranes for the FO process have attracted increasing attention in the recent decade [210]. The burgeoning TFNC membranes appear to be ideal candidates as future FO membranes because the highly porous and hydrophilic substrate made from electrospun nanofibrous scaffold is beneficial to alleviate the internal concentration polarization (ICP) effect. Early studies reported a wide range of polymers that were made into support layers for TFNC FO membranes via electrospinning, such as PES [211], PET [212], crosslinked PVA [213], interpenetrating PET/PVA [214], PAN/CA blend [215], etc. The replacement of traditional substrate from phase inversion with electrospun nanofibrous scaffold mitigates ICP efficiently and results in high permeation flux and energy saving. For example, a PES nanofibrous scaffold-supported FO membrane, reported by Song et al. demonstrated high water flux that was twice higher over a commercial FO membrane and a phase inversion FO membrane at all salt concentrations [211].

The recent trend related to performance enhancement of FO membranes includes two types of strategies: substrate modification either on the crude nanofibrous scaffold or on the nanofibers with/without the existence of additives; [71,216–221] and the introduction of an interlayer between the active layer and the nanofibers support [222–225]. For instance, a dual-layer composite nanofiber consisting of PVDF core layer and CA sheath layer, was fabricated into nanofibrous support via coaxial electrospinning, as shown in Fig. 14a [221]. The resultant FO membrane with improved mechanical stability and hydrophilicity achieved a water flux of 1.2 L/m²h and a low specific reverse salt flux of 0.03 g/L. Yu et al. introduced an interlayer of oxidized multi-walled carbon nanotubes (OMWCNTs) and graphene oxide (GO) onto a PVDF nanofibers support [224]. The interlayer provided both a transfer passage for water molecules and an effect on decreasing the polyamide layer thickness, leading to a super high water flux of 305.89 L/m²h and super low reverse salt flux of 0.37 g/m²h using 0.6 M NaCl

solution and deionized water as draw solution and feed solution, with a structural parameter of 82 μm . It could be noted that a unique FO membrane with a well-aligned nanofiber support layer was fabricated recently and exhibited a high water flux of 50.7 L/m²h with ultralow reverse salt flux under 1 M NaCl draw solution and deionized water feed solution (Fig. 14b) [226]. These enhanced performances were attributed to the aligned nanofiber substrate, which caused a thinner polyamide layer over the substrate with randomly oriented nanofibers, and therefore a decrease of mass transfer resistance and alleviated ICP effect.

Overall, electrospun nanofibrous support layers have been recognized as an effective alternative over conventional support layers for polyamide TFC membranes in the FO process, due to their improvement of water flux and their control of the ICP effect. Compared with the supports for RO membranes that require higher mechanical stability under the high-pressure operating conditions, the nanofibrous supports in the FO process have shown more practicality and a better chance for commercialization.

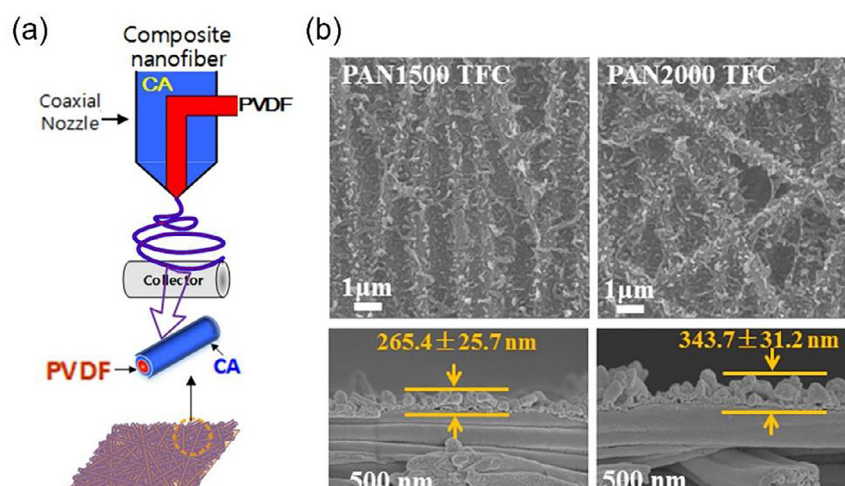
5 Top layer

With much attention being paid to the design and improvement of active layers to achieve effective water purification, the top layer has somehow been overlooked. However, the top layer will not only influence the purification efficiency, but also the durability of the membranes due to their antifouling and antimicrobial property.

Many types of foulants, including bacteria, biopolymers, natural organic matter, oils, proteins, particles, and salts, should be taken into consideration [227]. The foulants will cause a transient flux decline or pressure increase and a decrease in salt rejection [228]. The fouling to the membrane would cause inconvenience for practical operation and increase the operating costs due to the increased energy input to compensate the permeance decrease or the required membrane cleaning and replacement [46]. Biofouling is a major obstacle to membrane usage, which includes the attachment and growth of microorganisms [44].

The most common one is coating the membrane with an antifouling agent [229–233], which is assigned as the top layer. The top layer makes the membrane surface less favorable for foulant attachment by controlling the hydrophilicity to form a strong hydration layer to prevent attracting foulants [227], which plays a great role in water purification. The most common polymer used in the antifouling top layer is polyethylene glycol (PEG) based [234]. Various methods are involved to achieve the PEG incorporation, such as grafting to or forming a membrane by UV-light [235] or controlled radical grafting [236–238], and coupling to unreacted carboxylic acid/acetyl chloride groups on the membranes [239–242], or physical adsorption [243,244]. Bio-inspired chemistries, such as mussel-inspired polydopamine coatings [42,83,245–249] and chitosan-based coatings [250–252], as well as zwitterionic chemistries, including carboxybetaine [253–255], sulfobetaine [256–263] and phosphobetaine zwitterions [260,264], can also be used as antifouling coatings.

Another approach is deactivating the bacteria upon contact with the membrane surface [265], either by coating the membrane

**Fig. 14**

(a) Schematic diagram of the coaxial electrospinning technique to fabricate dual-layered CA/PVDF composite nanofiber support, and (b) surface view and cross-section SEM images of TFC membranes with aligned nanofiber support (left) and randomly orientated nanofiber support (right). Adapted with permission from Refs. [221] and [226]. Copyright © 2018 and 2020 Elsevier B.V. All rights reserved.

with antimicrobial agents or embedding antimicrobial agents within the membrane. Quaternary amines can be utilized as the antimicrobial coating since they can puncture the cell wall [266–270], in which the alkyl chains with 6–8 carbons are the most effective ones [271,272]. What is more, the incorporation of silver nanoparticles [273,274] or gold nanoparticles [275] can also create antimicrobial surfaces.

In addition, the combination of antifouling and antimicrobial strategies, incorporating one antifouling and one antimicrobial material, has been developed to reduce membrane fouling effectively [276–281]. A unique method was explored as a coating that could switch reversibly from an antifouling mode to an antimicrobial mode. These coatings are zwitterionic in nature, which could expose the quaternary amine under certain conditions to gain antimicrobial property [282–284].

6 Conclusion and outlook

With the advantages of satisfying performance, cost-effectiveness, controllable membrane structures, and properties as well as scalable production capacity, polymers are the dominant current materials for water purification membranes and seem to have the potential for further improvement. Nanotechnology has brought new vitality to membrane separation by the construction of nanofibrous membrane systems, the incorporation of nanoparticles and nanofibers into the membrane matrix, and the understanding and design of nanoscale structures. Some typical membranes for MF, UF, NF, RO FO, and MD operations are summarized in Table 1, which provides a comparison of membrane components and performance between the membranes based on conventional polymer matrix and/or electrospun nanofibrous scaffolds.

Conventional MF and UF membranes as well as the traditional support layer for TFC membranes generally originate by the phase inversion process from a wide variety of polymers, which could be further modified by using polymer blends and/or (nano) additives.

To address the main challenge for MF and UF membranes, which is membrane fouling, various strategies have been developed.

TFC membranes for NF, RO, and FO operations typically possess three layers that can be designed separately. Previous studies paid most attention to the polyamide active layer improvements by updating monomers and enhancing selective layer properties, like antifouling property, chlorine resistance, long-term stability, etc. A recently emerging strategy, by utilizing the introduction of an interlayer between the active layer and the support layer, has offered a potential approach to upgrade TFC membrane efficiently and showed the possibility to break the trade-off limitation, while the difficulties in cost-effective fabrication and scalability have remained to be practical challenges [81].

Electrospun nanofibrous membranes with unique properties exhibit good water purification performance in MF, UF, NF, RO, MD, and in particular, the FO process, such as very high water flux, high rejection ratio, low operation pressure, and recyclability. The low cost, environmentally benign, and energy-saving features are also attractive advantages of the electrospun nanofibrous membranes that make them good candidates for future drinking water purifications. Another cost-effective model, TFNC membranes, has demonstrated excellent performance in heavy metal absorption, oil/water separation, desalination, and membrane distillation. A recent review has provided discussions of water filtration membranes made from nanocelluloses that are sustainable materials [286]. Moreover, the understanding and construction of (nano) structures in the membrane, such as directed water nanochannels, could stimulate future high-performance membranes designs. However, electrospun nanofibrous membranes have so far suffered from the deformation upon compaction, making them more suited only for low-pressure separation processes at present.

The development of the support layer of TFC membranes should be considered as important progress made in the past decade. For the conventional support layer made through the

Table 1

Summary examples of polymer-based membranes for water purification.

Process	Selective layer	Support layer	Filtration performance	Membrane design	Refs.
MF	crosslinked CA/PEI blend		Pure water flux = 10–50 ml/cm ² min, 69 kPa Maximum absorption = 7.42 mg/g dry membrane (Cu ²⁺), 86.6 mg/g dry membrane (BSA)	A modified MF membrane prepared from CA/PEI blend	[31]
MF	PAN nanofibers		Water flux = 225.69 kg/m ² h (pressure ≤ 980 Pa) Separation factor for 10 μm particles = 93% Tensile strength = 4.87 MP	Self-supporting nanofibrous membrane with high water permeability and mechanical strength	[117]
MF	PVA/PAN interpenetrating nanofibers		Water flux = 1030 ± 28 L/m ² hpsi Cr ⁶⁺ adsorption = 133 mg/ (g PAN nanofibers) Ultimate tensile strength = 132.7 ± 6.3 MPa Young's modulus = 8.1 ± 0.1 MPa	Free-standing interpenetrating nanofibrous composite membranes prepared by two-nozzle electrospinning	[118]
MF	PAN nanofibers	PET	Flux ~ 1.5 L/m ² h Retention of microparticles of 0.20–1 μm ~ 93% Bacterial retention: log reduction value = 6	High-flux electrospun nanofibrous membranes	[120]
MF	Surface-functionalized electrospun PAN nanofibrous membrane		Water permeability = 430 L/m ² hpsi Retention of bacteria = 99.99% Retention of bacteriophage = 99.99%	PAN electrospun nanofibrous MF membrane functionalized with poly(dual- and tri-vinyl monomers)	[124]
UF	CA-CNF (Cellulose acetate-cellulose nanofiber)		Water flux ~ 102 L/m ² h (transmembrane pressure = 10 psi) BSA selectivity = 85%	Membranes with hydrophilic nanochannels created by the embedment of cellulose nanofibers into the polymer matrix	[134]
UF	Nanocellulose/PAN	PAN nanofibers on PET mat	Pure water permeability = 1508 L/m ² h MPa BSA rejection ratio = 98.4% Antifouling	High-flux antifouling nanofibrous composite UF membranes with negatively charged water channels	[135]
UF	PVA/MWNTs	crosslinked PVA nanofibers on PET support	Flux rate = 330 L/m ² h (feed pressure = 100 psi) Organic solute rejection rate = 99.8%	High flux three-tier composite membrane based on a nanofibrous substrate with hydrophilic nanocomposite coating	[125]
UF	Electrosprayed PVA	PAN nanofibers	Flux = 347.8 L/m ² h (feed pressure = 0.2 MPa) Organic rejection rate = 99.6%	TFNC membranes prepared by electrospraying technique combined with solution treatment	[129]
UF	PVA/carbon nanotubes	PAN nanofibers on PET support	Water flux = 60 L/m ² h (pressure = 20 kPa) Oil rejection = 95% In-air superhydrophilic surface	A superwetting thin-film nanofibrous composite membrane with excellent antifouling and self-cleaning properties for oil/water separation	[137]
UF	Self-assembled PS-b-PEO membrane		Pure water flux ~ 800 L/m ² hbar BSA rejection = 67% γ-globulin rejection = 99%	Self-assembled PS-b-PEO membranes	[179]
NF	PA/Ca(HCO ₃) ₂	PES	Water permeance = 13.4 ± 0.3 L/m ² hbar Na ₂ SO ₄ rejection = 99.9% Antifouling Flux recovery ~ 90.0% after cleaning	TFC membrane with the incorporation of Ca(HCO ₃) ₂ in the polyamide layer	[70]
NF	PA/capsaicin derivative	PSF UF membrane	Water flux = 115 L/m ² h (pressure = 5.0 bar) Na ₂ SO ₄ rejection > 98.0% Antifouling Flux recovery ~ 100% after cleaning	TFC membrane modified by hydrophilic capsaicin-mimic moieties	[71]

(continued on next page)

Table 1 (continued)

Process	Selective layer	Support layer	Filtration performance	Membrane design	Refs.
NF	PA	PVA interlayered PES UF support	Water permeance = 31.4 L/m ² hbar Na ₂ SO ₄ rejection = 99.4%	TFC membrane with a PVA interlayer between the PA layer and the support	[86]
NF	PA	Single-walled carbon nanotubes/PES composite support	Permeance = 53.5 L/m ² hbar Na ₂ SO ₄ rejection > 95%	TFC membrane with PA layer prepared with nanoparticles as sacrificial templating material	[90]
NF	PA	PVDF nanofibers on PET support	Permeate flux = 26.9 L/m ² h MPa MgSO ₄ rejection rate ~ 97% NaCl rejection rate ~ 76%	TFC membrane fabricated with a PVDF tree-like electrospun nanofiber membrane containing directed water channels	[206]
RO	PA	interlayer/(PAN UF membrane)	Water flux = 23.0 ± 4.8 L/m ² h (operating pressure = 15.5 bar) Maximum NaCl rejection = 98.2 ± 0.6%	Tailor-made PA-based membranes based on molecular layer-by-layer (mLbL) assembly	[65]
RO	PA/(cellulose nanofibers)	PS	Flux = 29.8 L/m ² h (pressure = 1.5 MPa) NaCl rejection = 96.2% Improved chlorine resistance	TFC membrane with the polyamide layer with TEMPO-oxidized cellulose nanofibers	[77]
RO	PA	TFNC UF membrane: cellulose nanofibers/PAN nanofibers/PET mat	Flux = 28.6 L/m ² h (operating pressure = 0.7 MPa) NaCl rejection ratio = 96.5%	Thin-film nanofibrous composite (TFNC) RO membranes fabricated with fibrous substrate CN/PAN/PET	[204]
FO	PA	CA/PVDF nanofibers	Water flux = 31.2 L/m ² h Specific reverse salt flux = 0.03 g/L Structural parameter = 190 μm (0.5 M NaCl as draw solution, deionized water as feed)	TFC FO membrane with an electrospun nanofibrous support mat fabricated via coaxial electrospinning	[223]
FO	PA	PSF support on PET substrate	Water flux > 18 L/m ² h Salt rejection > 97% Structural parameter ~ 492 μm (1.5 M NaCl as draw solution, pure water as feed)	TFC FO membrane	[285]
FO	PA	GO/ OMWCNTs interlayered PVDF nanofibrous support	Water flux = 305.89 L/m ² h Reverse salt flux = 0.37 g/m ² h Structural parameter = 82 μm (0.6 M NaCl as draw solution, deionized water as feed)	A composite membrane with a graphene oxide and oxidized multi-walled carbon nanotubes interlayer between the PVDF nanofibrous support and the PA layer	[224]
FO	PA	well-aligned PAN nanofibers	Water flux = 50.7 L/m ² h Specific reverse salt flux < 0.2 g/L Structural parameter ~ 86 μm (1 M NaCl as draw solution, deionized water as feed)	TFC-FO membrane with well-aligned nanofibers substrate	[226]
MD	PH nanofibers	PET microfibers	Water flux = 79.21 ± 4.17 L/m ² h NaCl rejection > 99.9% (3.5 wt% NaCl as feed, transmembrane temperature = 40 °C in DCMD)	Hierarchical fibrous composite MD membranes	[162]
MD	PS/(SAN nanofibers)	PAN nanofibers	Permeate flux = 84.4 kg/m ² h Salt rejection = 99.9% Water contact angle (WCA) = 155.9° (35 g/L feed, transmembrane temperature = 40 °C in DCMD)	Dual- and triple-layer composite MD membranes fabricated via electroblowing and air-assisted electrospraying	[165]
MD	Electrospun PVDF/SiO ₂	PVDF nanofibers	Permeation flux = 24.6 ± 1.2 kg/m ² h Rejection ratio = 99.99% Water contact angle (WCA) > 150° (3.5 wt% NaCl feed, transmembrane temperature = 40 °C in DCMD)	Highly robust superhydrophobic dual-layer MD membranes fabricated via electrospinning	[163]

(continued on next page)

Table 1 (continued)

Process	Selective layer	Support layer	Filtration performance	Membrane design	Refs.
MD	PP	PVDF nanofibers	Permeate vapor flux = 53.1 kg/m ² h Water contact angle (WCA) = 153.6° (3.5 wt% NaCl feed, transmembrane temperature = 40 °C in DCMD)	Superhydrophobic dual layer nanofibrous composite MD membrane with a biomimetic and integrated porous skin layer	[164]
MD	PSF nanofibers/PTFE nanoparticles		Permeate flux = 39.5 kg/m ² h Permeate electrical conductivities < 7.145 μS/cm Rejection ratio = 99.99% Water contact angle (WCA) = 153° (30 g/L NaCl feed, transmembrane temperature = 60 °C in DCMD)	PTFE/PSF mixed matrix electrospun nanofibrous membrane for MD	[151]

phase inversion process, the support layer properties, such as pore size and hydrophobicity, not only affect the separation properties of the support layer itself but also play a vital role in selective layer formation, subsequent membrane morphology/structure and the ultimate membrane performance. Although some efforts have been made to understand the mechanisms and to adjust support layer properties, such considerations still deserve fundamental and systematic investigation. There remains a need to understand, improve and design advanced support layers for superior TFC membranes, based on fundamental principles.

TFNC membranes with electrospun nanofibrous scaffolds as support layers have demonstrated excellent performance over conventional TFC membranes in RO and FO processes, due to their high permeation flux and high rejection ratio. TFNC membranes are promising, especially in the low-pressure and energy-saving FO operations, because the high porosity and the interconnected pores help to alleviate the ICP effect. Whilst more research on improving mechanical properties and mass production methods is expected for large-scale applications of electrospun nanofibrous membranes in the future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

T.L. acknowledges support from the NSF (CHE1904397 and EFR12132178) and the University of Akron.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.giant.2022.100099](https://doi.org/10.1016/j.giant.2022.100099).

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