



Forward osmosis membranes for desalination and wastewater treatment: Review of recent advances in electrospun nanofiber-based substrates, challenges, and future research recommendations

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ABSTRACT

Forward osmosis (FO) technology has great potential for water purification applications but has not been commercialized on a large scale due to the lack of a specific membrane structure. The main problem with FO technology is the internal concentration polarization (ICP) that occurs within membrane substrates. Electrospun nanofiber (ESNF) based membrane substrates are considered a promising class of materials for thin-film composite (TFC) membranes for FO for water and wastewater treatment applications due to their unique properties, such as high porosity with interconnected pore structure. The main objective of this work is to review recent developments in the fabrication of ESNF-based substrates using different methods to develop TFC-FO membranes. Some potential fabrication methods are highlighted in this review to help researchers scale up FO membrane technology. To further advance the use of ESNF-based TFC-FO membranes in various water treatment applications such as desalination, heavy metal ion removal, and bacteria removal, some important challenges such as ICP, fouling, lack of mechanical strength, etc. need to be solved. Therefore, it is expected that interest in this process will continue to increase with the help of advanced nanotechnologies such as hybrid membranes, surface modification, cross-linking, layer-by-layer deposition of polyelectrolytes, etc.

1. Introduction

There is a great demand for modern, sophisticated and eco-friendly techniques that can remove these dangerous substances, such as metallic waste, medical waste, and other organic pollutants from water and improve water quality to reusable, clean, and safe drinking water ([51,48,90]). Membrane-based separation processes are leading technologies for wastewater treatment and desalination [31,32,49,59,76]. Forward osmosis (FO) is considered to be one of the most effective solutions for wastewater treatment. FO is an osmotically driven membrane separation process widely used in water purification tasks and other applications, such as waste processing in the medical industry, agricultural processes, beverage industries, and osmotic power generation for desalination [2,50,77]. Research related to FO is gaining considerable

attention among researchers, mainly due to its effectiveness in the water purification process and its ability to solve the problem of water scarcity [12,29,33]. Additionally, FO offers other advantages, such as cost-effectiveness, better performance, and simple implementation [55, 86]. The Conventional FO membrane follows the method of reverse osmosis (RO) membrane using a phase-inversion technique to form the substrate layer with finger-like and sponge-like pores. The key objective of FO technology is to fabricate a FO membrane with greater permeability, good rejection of salts and foulants, and stable water flux during long-term operation. The thin-film composite (TFC) membrane, a semi-permeable membrane for FO, has high permeate water flux and salt rejection. One of the major drawbacks of the FO technology is the internal concentration polarization (ICP) that occurs within the membrane support layer [69]. The structural characteristics of the FO membrane

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support layer play a crucial role in controlling the problem of ICP [89] [46]. Therefore, an ideal substrate layer of a FO membrane needs to possess certain important characteristics, such as high porosity, low tortuosity, and low thickness. These parameters are responsible for enhancing the water flux and decreasing the intensity of the ICP [43,75]. Electro. Electrospun nanofiber (ESNF) based membrane supports are considered a promising class of materials for TFC-FO membrane supports due to their unique features, such as high porosity with interconnected pore structure [24,27]. In contrast to previous reviews, the main objectives of this article are as follows: (i) to emphasize recent advancements in the fabrication of ESNF-based substrates for the purpose of designing TFC-FO membranes that can achieve high-performance and cost-effectiveness, (ii) to assess and examine the potential of ESNF-based TFC-FO membranes for various water purification applications, including desalination, removal of heavy metal ions, and bacterial removal performance, with the aim of addressing water scarcity and environmental pollution, (iii) to identify promising fabrication methods that can assist researchers in scaling up FO membrane technology, to facilitate the widespread adoption of FO membranes in different industries and applications, (iv) to address significant challenges such as ICP, fouling, and lack of mechanical strength, which are

crucial for enhancing the performance and durability of ESNF-based TFC-FO membranes, and (v) to provide recommendations for future modifications of ESNF substrates to overcome the aforementioned challenges and achieve desired performance and properties for various FO membrane applications.

2. FO principles

Osmosis is the spontaneous transport of solvent molecules (mostly water) across a semi-permeable membrane from a feed solution (FS) of high solvent concentration/higher chemical potential (i.e., low solute concentration) to a stream of lower solvent concentration/lower chemical potential (i.e., high solute concentration). A solution with low chemical potential is termed the draw solution (DS) [20,36]. An ideal semi-permeable membrane allows the passage of solvent molecules and rejects the passage of solute molecules/ions. Osmotic pressure stops the solvent (i.e., water) transport across the semi-permeable membrane when applied to the draw solution. This osmotic pressure (π) of a solution can be calculated using the Van't-Hoff equation given below:

$$\pi = icRT$$

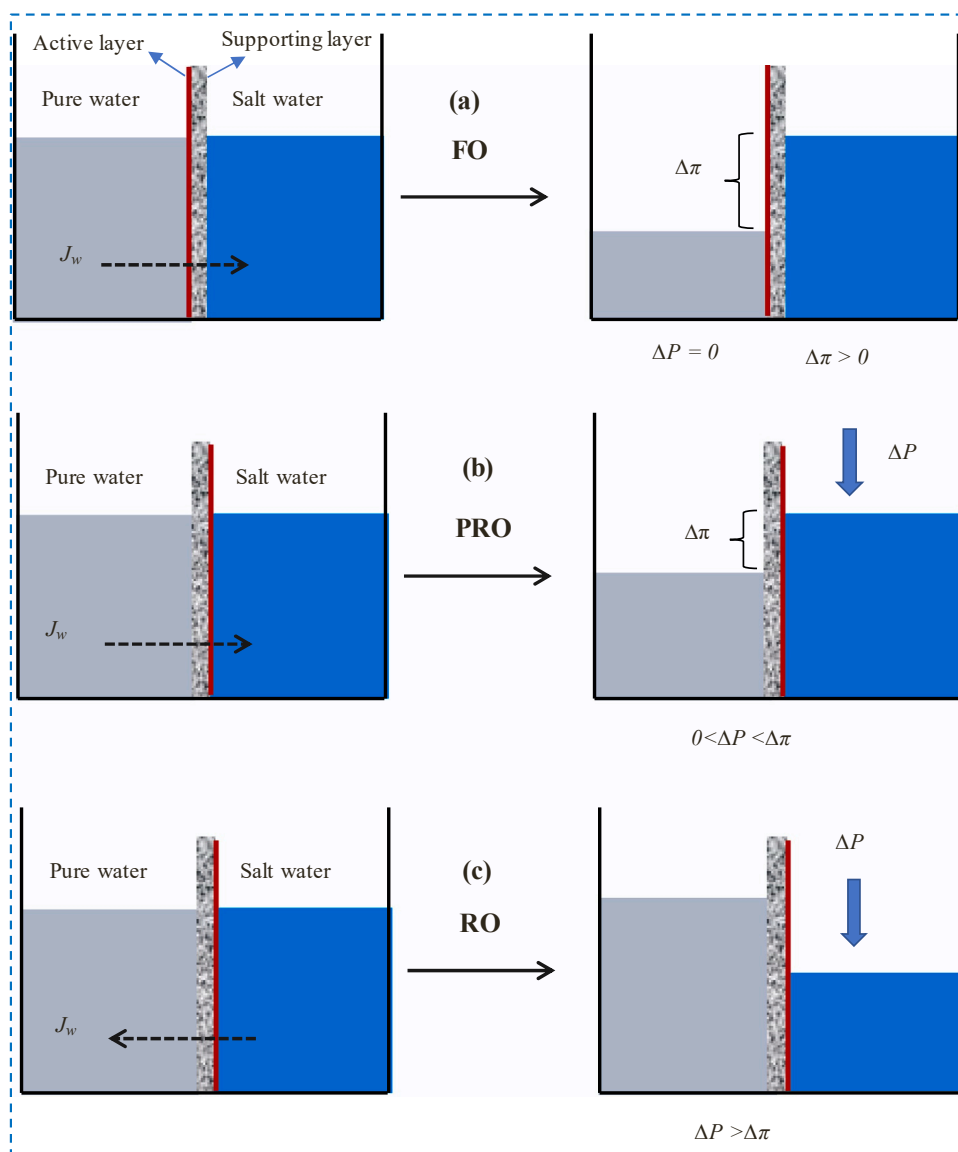


Fig. 1. Schematic representations of different osmotic processes [7,20].

where i is the number of the Van 't Hoff factor of osmotically active solute molecules in the solution), c is the molar concentration (mol. L^{-1}), R is the universal gas constant ($8.31441 \text{ J.K}^{-1}.\text{mol}^{-1}$) and T is the absolute temperature (K). As shown in the equation, the osmotic pressure differential depends on the concentration of each solution. The osmotic pressure of seawater at 25°C is between 25 and 33 bar because the NaCl concentration differs from 3.0 to 4.0 wt% in different locations.

Fig. 1 represents three possible osmotic processes that occur from the contact of fresh water and salty water through a semi-permeable membrane [7,20]. FO (Fig. 1a), or a naturally occurring process, occurs when the only driving force of water flux (J_w) via the semi-permeable membrane is the osmotic pressure gradient ($\Delta\pi$) between the two solutions. In this FO process, $\Delta\pi$ is non-zero and positive, i.e., $\Delta\pi > 0$, and the solutions are either unpressurized or pressurized at the same magnitude, making $\Delta P = 0$. When a hydrostatic pressure ΔP is applied on the more concentrated side (salt water), the permeated water is retarded and eventually ceases when pressure increases gradually. Mathematically, the water flux (J_w) will stop when ΔP equals $\Delta\pi$. At any stage when the ΔP is between 0 and $\Delta\pi$, the water still flows into the more concentrated side by the $\Delta\pi$ because this $\Delta\pi$ remains greater than ΔP . This phenomenon is called Pressure Retarded Osmosis (PRO, Fig. 1b). In this PRO, the feed solution flows to the side of the salt (draw) solution as long as $\Delta\pi$ remains larger than ΔP . When the applied pressure ΔP on the salt (draw) solution side is greater than the osmotic pressure $\Delta\pi$, the direction of the water flux (J_w) occurs from the salty water to the fresh water side through the membrane, resulting in a negative flux. This process is referred to as Reverse Osmosis (RO, Fig. 1c) since the water flows opposite to the natural osmotic process. RO has been widely used for the desalination of seawater.

The relationship between the three illustrations explained above in terms of water flux and pressures are demonstrated in Fig. 2a [7]. Potential flux across the semi-permeable membrane is calculated as a function of the osmotic pressure difference ($\Delta\pi$, in bar), the hydrostatic pressure difference (ΔP , in bar), and the membrane intrinsic water permeability coefficient (A) in $\text{L. m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$ (LMH):

$$J = A (\Delta\pi - \Delta P)$$

In summary, the FO process is based on an essential parameter, namely the osmotic pressure gradient, which acts as the driving force to propel water in such a way that the water penetrates into a semi-permeable membrane. Water flows through the membrane from an FS to a DS. Thus, no further energy is needed for FO; energy could be harvested by PRO, while energy must be provided for RO [1,69].

A discussed earlier, the major issue with FO technology is the ICP

that develops within the membrane substrates [69]. The dilutive ICP develops because of the dilution of concentrated DS solutes across the supporting layer, while the precipitation of the molecules in FS across the active layer (AL-FS, FO mode) allows for a decrease in water flux. Generally, concentrative ICP develops in PRO orientation (active layer facing the DS, AL-DS). In this phenomenon, solutes from DS accumulate at the interface between the substrate layer and the active layer, decreasing the effective driving forces and causing a reduction in the water flux. Fig. 2b shows the mechanisms of both dilutive ICP and concentrative ICP [98].

3. ESNF-based substrates for TFC-FO membranes

Since the early 1990s, electrospinning has been considered one of the simplest and potential technologies for fabricating electrospun nanofiber (ESNF) supports. As shown in Fig. 3, a standard electrospinning setup consists of a high-voltage power supply, a syringe pump (a dope-driven system), a spinneret with a blunt-tipped metallic needle, and a grounded plate collector for the fabrication of the nanofibers [34,39]. The effects of the intrinsic properties of polymeric dopes, operational conditions, and surrounding conditions are displayed. The use of electrospun nanofibers in different membrane-based separations for water and wastewater treatment applications has received significant interest in the last decade. Several previous reports have been published on the use of ESNF-based membranes in microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), RO, and membrane distillation (MD) [38,70,81]. The advantages of ESNF-based membranes for the purification of water and wastewater management have been validated by previous works [35,67]. Considering the advantages, such as the high porosity and interconnected pores of the ESNF mats, some reports have used ESNF-based substrates for the fabrication of TFC-FO membranes [65,80]. Different polymeric materials have been extensively implemented as ESNF support materials for the fabrication of TFC-FO due to their superior attributes, such as robust mechanical properties, high chemical resistance, thermal stability, and better pH tolerance [27,52,74]. As Fig. S1 (in the supporting information) demonstrates, the number of published research articles on ESNF-based substrates for FO applications has increased significantly, especially in recent years (2014–2023); consequently, there is a need to monitor the current results and identify future challenges.

In 2011, a TFC membrane based on ESNF was produced for the first time for FO by the Song et al., group [80]. Various approaches have been introduced to enhance the performance of ESNF-based TFC-FO membranes, including different fabrication approaches, hydrophilic polymer

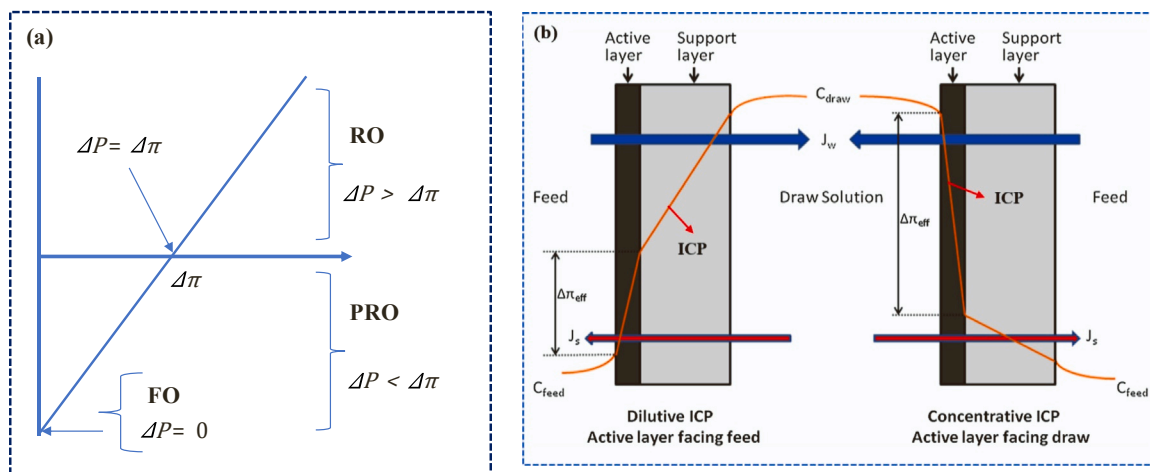


Fig. 2. (a) Direction of water flu as a function of applied pressure in FO, PRO, and RO. (b). Dilutive and concentrative ICP Illustration 'reproduced with permission from Zhao et al. [98]'

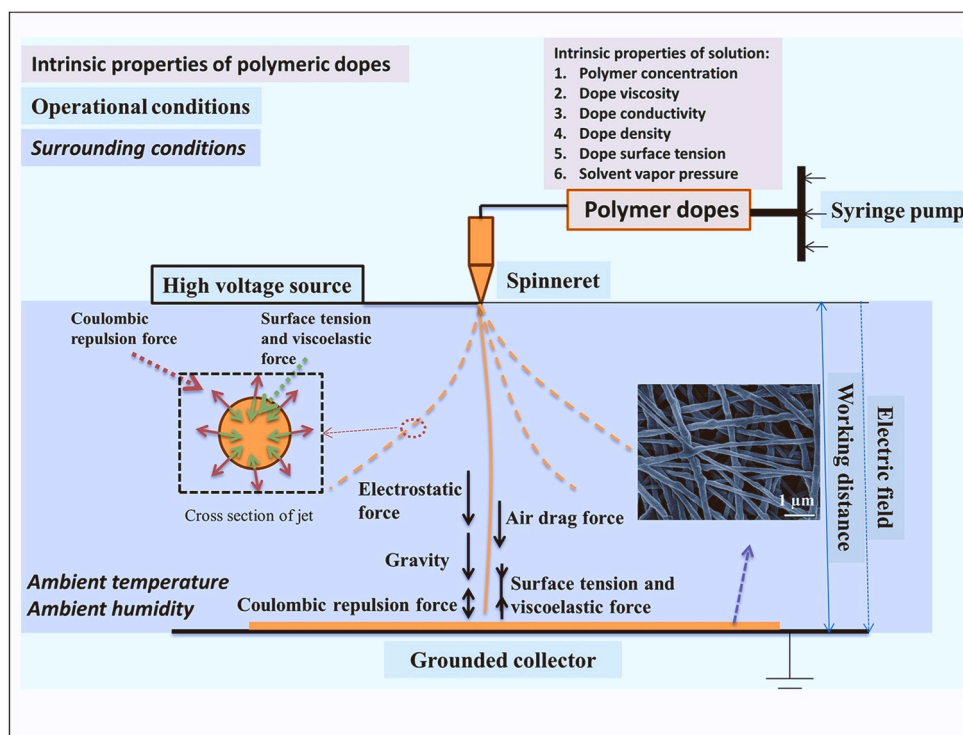


Fig. 3. Schematic illustration of the preparation of electrospun nanofibers 'reproduced with permission from Liao et al. [39]

blending, coating, cross-linking, thermal treatment, nanoparticle incorporation, surface modification, layer-by-layer polyelectrolyte deposition, etc. Water permeability (A), solute permeability (B), and internal structure parameter (S) are important parameters for the performance of FO. Therefore, the development of ENSF-TFC FO membranes will be evaluated based on the A , B , and S parameters, which are discussed in the following subsections.

3.1. Single polymeric ENSF supports

The most common polymeric materials employed in ENSF fabrication are polysulfone (PSf), polyether sulfone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polyvinyl chloride (PVC), polyvinyl alcohol (PVA), cellulose acetate (CA), polyethylene (PE), chitosan, and polyimide due to their chemical stability, mechanical strength, and flexibility. Song et al. prepared a TFC-FO membrane (NC-FO) with a scaffold-like PES-based ENSF substrate that holds incredible compensations over conventional substrates (home-made phase inversion PI-FO) [80]. Fig. 4a shows the SEM images of the NCFO and PI-FO substrates. This nanocomposite FO membrane works well in both FO and PRO modes, as the low tortuosity significantly reduces the diffusive resistance in the FO mode. As can be seen from Fig. 4b, the TFC-FO membrane with home-made PI-FO substrate shows a significant flux difference (red line), while the TFC-FO membrane with ENSF-based NC-FO substrate (green line). In another study, PES and PSf-based ENSF substrates were successfully fabricated onto a commercial polyester (PET) nonwoven fabric. After that, the PA layer was polymerized in situ onto the ENSF support through the IP process [3]. These developed ENSF-based TFC membranes achieved two to five times higher osmotic water fluxes with up to 100 times lower salt flux than the commercial HTI-CTA membrane. The PVDF-based ENSF substrate was successfully fabricated to make a TFC-FO membrane [83]. In this study, PA thin films were deposited on two PVDF ENSF substrates (ES-1 and ES-2) with different pore sizes and surface roughness values. Fig. 4c shows the AFM images of nanofiber-based TFC membranes. These differences between the PA layers are attributed to the different degrees of cross-linking

during the IP. The best TFC membrane in this work showed a water flux of 30.4 LMH and a reverse salt flux of 0.21 g/L [83]. These results revealed that the ENSF-based TFC membranes have good potential as substrates because of their superior porous and interconnected open structure. Huang et al. fabricated nylon 6, 6 nanofibers via electrospinning and used them as a support structure for the TFC-EO membrane [25]. The TFC-0.75 membrane showed 1.5-fold and 2-fold higher water flux in PRO and FO mode compared to the commercial HTI membrane. Furthermore, the TFC-0 membrane showed 2- and 10-fold lower reverse salt flux in PRO and FO mode, compared to commercial HTI membrane, respectively, due to their low structural parameter (tight polyamide), which decreased internal CP.

To reduce ICP, a self-sustained PAN ENSF-supported TFC-FO membrane (PA/PAN-eTFC) was developed [60]. In this study, the ENSF substrate was prepared without any backing layer and then laminated by a paper lamination. Fig. 4d and e show the digital photograph and SEM morphology of the prepared PAN ENSF substrate, respectively. The prepared PA/PAN-eTFC membrane showed a low $S=168\ \mu\text{m}$, high water flux (57 LMH), and high permselectivity ($A=1.47\ \text{LMH}/\text{bar}$, $B=0.278\ \text{LMH}$) (see Fig. S2a) [60]. This membrane showed a rejection of tetracycline (TC) and a 15–22% water recovery after 7 h running in the FO–MD hybrid process.

A commercially available unsupported nanofiber (DuPont PES-based ENSF) was used to prepare a robust and high-performance TFC-FO membrane [10]. This commercial DuPont PES TFC membrane exhibited 200% and 130% higher water flux in the FO mode and the PRO mode compared to the HTI TFC membrane [10]. Moreover, DuPont PES is illustrated as a better strength-supportive material to support the polyamide selective layer, compared to typical electrospun materials. The DuPont PES TFC membrane was also found to show a 2-fold water flux and one-tenth the reverse solute flux compared to a commercial TFC FO membrane.

Some studies have used ENSF-based FO membranes to treat antibiotic-containing wastewater. To investigate the antibiotic removal mechanism using ENSF-based FO membranes, Zhang et al. fabricated a TFC-FO membrane supported by the PSf ENSF substrate [97]. In this

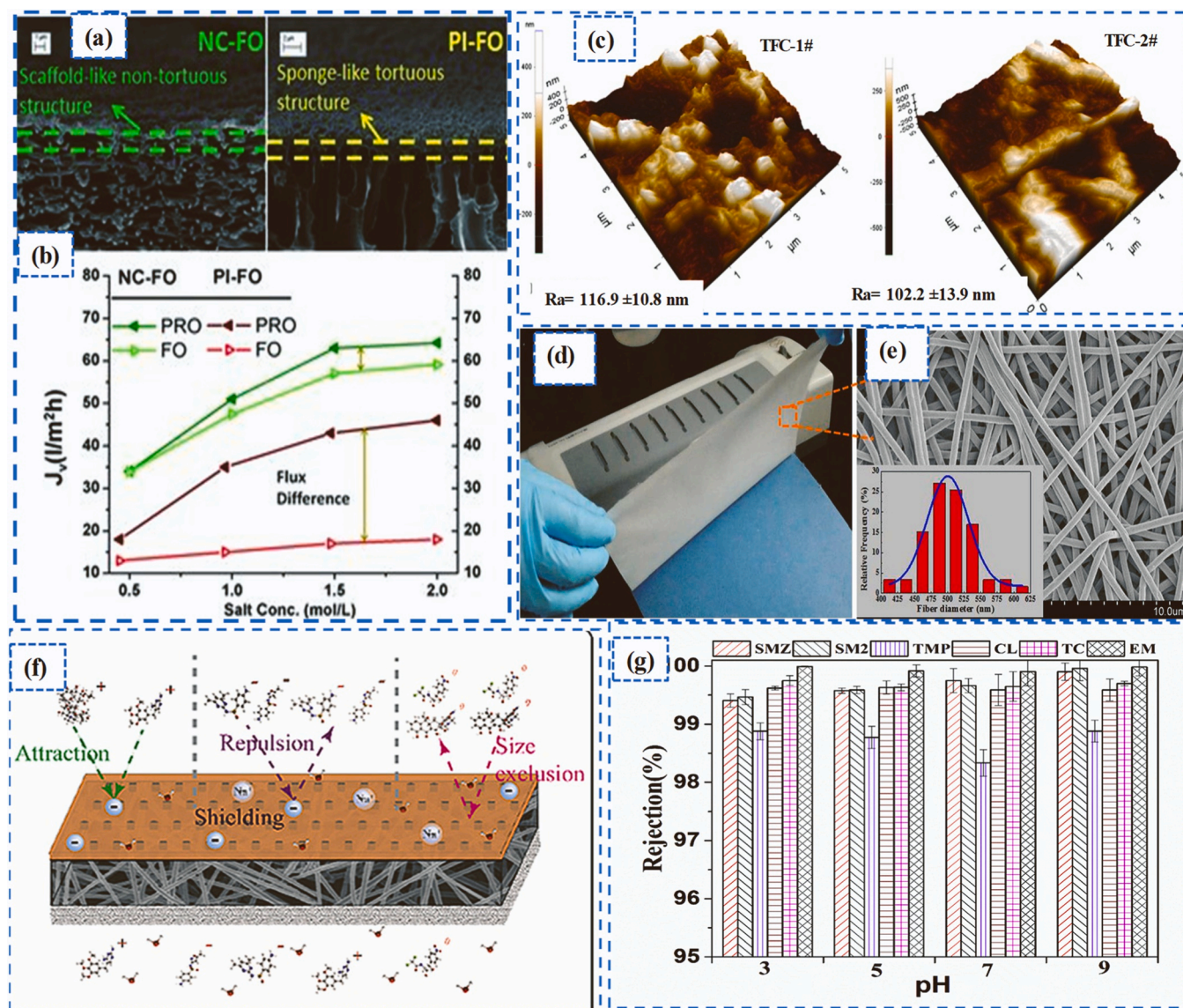


Fig. 4. (a) Cross-sectional SEM image of an ESNF substrate (NC-FO) and a home-made phase-inversion PES substrate (PI-FO) 'reproduced with permission from Song et al. [80]'. (b) Water flux in both FO and PRO orientations 'reproduced with permission from Song et al. [80]'. (c) AFM images of the two prepared ESNF-based TFC membranes (TFC-1# and TFC-2#) 'reproduced with permission from Tian et al. [83]'. (d-e) Photograph and SEM image of prepared laminated PAN ESNF support 'reproduced with permission from Pan et al. [60]'. (f) The mechanism for removing antibiotics by the ESNF-based TFC-FO membrane under various test conditions 'reproduced with permission from Zhang et al. [97]'. (g) Different antibiotic rejections using the developed ESNF-based TFC membrane 'reproduced with permission from Zhang et al. [97]'.

study, the rejection of six differently charged antibiotics, namely sulfamethoxazole (SMZ), sulfamethazine (SM2), trimethoprim (TMP), erythromycin (EM), tetracycline (TC), and chloramphenicol (CL), by prepared TFC-FO (NCFO) membranes was investigated. It was found that the rejection of antibiotics is mainly determined by electrostatic interactions and steric hindrance (see Fig. 4f). The developed NCFO membrane showed significant performance with a water flux of 49 LMH, and the removal of all antibiotics was greater than 98% (Fig. 4g). Miao et al. [54] developed an asymmetric and free-standing FO membrane using p-aramid nanofibers (Dried Kevlar@49 fibers, Dupont™). The results showed that the developed membrane had a high value of FO water flux, better tensile strength, and thermal performance. The structure of the p-aramid and the proposed approach for the membrane preparation of the FO process are illustrated in Fig. S2c-d.

3.2. Polymer blend-based ESNF substrates

It has been widely reported that blended membranes show higher permeability than membranes prepared from a single polymer [27,64,75]. Generally, when hydrophilic and hydrophobic polymers are combined, hydrophobic will be considered the prominent material for fabricating ESNF substrates to achieve excellent mechanical features. Hydrophilic compounds can be used in lower concentrations to generate a hydrophilic surface for the ESNF substrates, which is essential for increasing the diffusion of solute and solvent, which can help reduce the ICP problem. Several blended polymer-based ESNF substrates were developed to alter the diameter of the fiber, porosity, and roughness of the substrate. Hoover et al. designed TFC membranes composed of both the ESNF polyethylene terephthalate ESNF layer (ePET) and a phase-separated PSf layer [23]. The cross-sectional SEM image of Fig. 5a and b show the successful casting of the PES layer on the prepared ePET layer. The developed TFC membrane showed the transport properties of

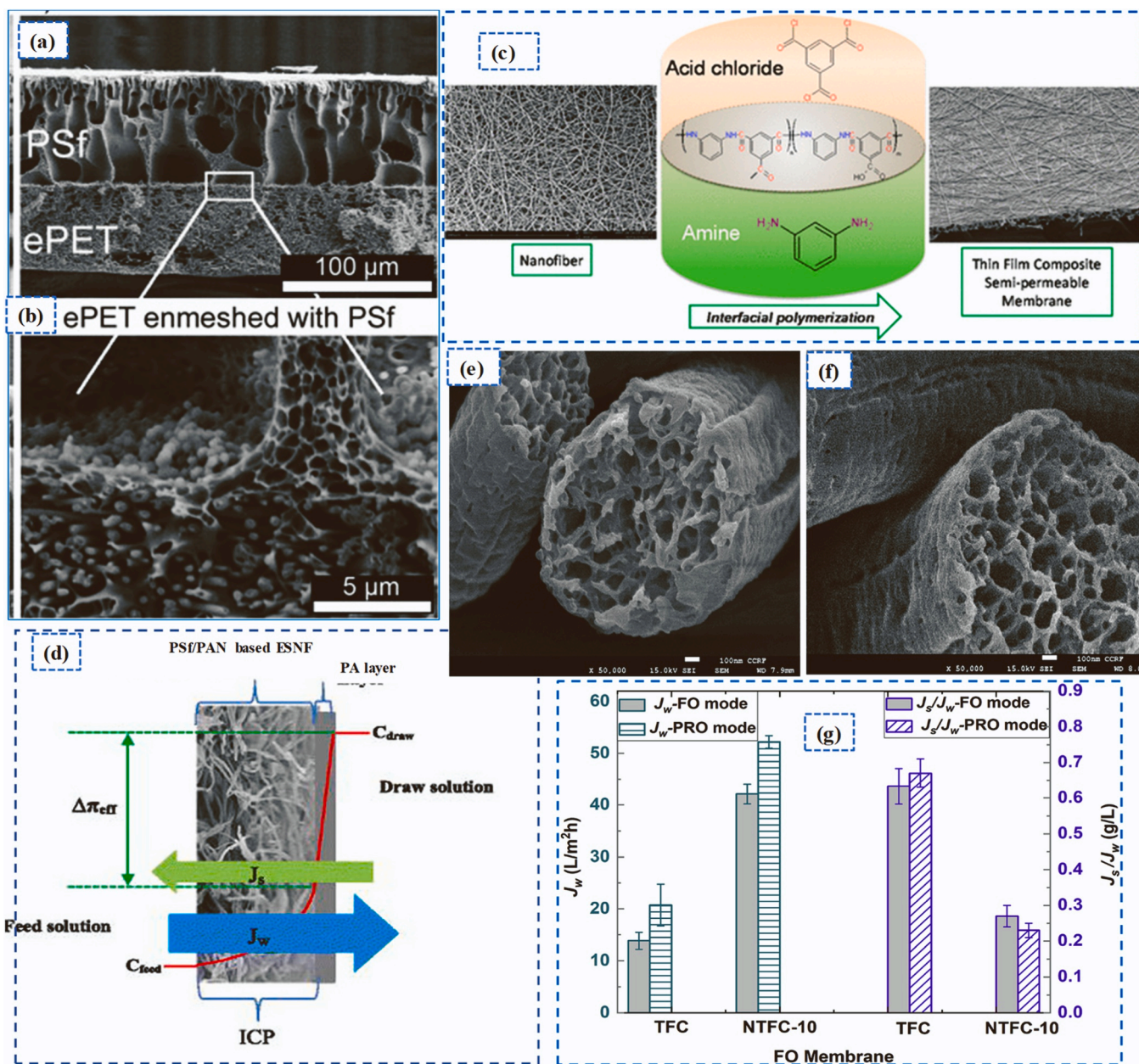


Fig. 5. (a–b) Cross-sectional SEM images of the developed blend (ePET/PSf) substrate ‘reproduced with permission from Hoover et al. [23]’. (c) Preparation PAN/CA ES NF supported TFC membrane ‘reproduced with permission from Bui et al. [6]’. (d) PSf/PAN ES NF-based TFC-FO [75]. (e–f) SEM cross-sectional image of pristine PES ES NF and PES/PAN blend ES NF, (g) FO performance of developed PES/PAN ES NF based TFC membranes (NTFC-FO) ‘reproduced with permission from Kallem et al. [27]’.

the active and supporting layer with a water flux of 1.13 LMH bar⁻¹, a salt flux of 0.23 LMH, and a structural parameter of 651 μm. Furthermore, using the ES NF layer in the substrate improved the membrane resistance to delamination at high cross-flow velocities [23].

To achieve an effective structure to fabricate a high flux FO membrane, hydrophobic polyethylene terephthalate/hydrophilic polyvinyl alcohol (PET/PVA) interpenetrating network blend ES NF was designed [82]. As shown in Fig. S3a, the wettability property of the composite layer was improved with an increase in the PVA content. The water flux of the FO membrane increased significantly with the increase of PVA content in the ES NF layer (Fig. S3b). The FO membrane with a PET/PVA ratio of 1/4 showed the highest water flux (47.2 LMH) and the low salt flux (9.5 gMH). The enhancement of the water flux and the reduction in the salt flux were attributed to the increase in the wettability of the support layer and the facile water pathway. PAN and CA blended

hydrophilic ES NF substrates were successfully fabricated and used for TFC membrane preparation [6] (see Fig. 5c). This novel PAN/CA ES NF-supported TFC membrane showed a water flux two to three times higher water flux and a 90% reduction compared to a commercial HTI FO membrane.

Shokrollahzadeh et al. explored the impact of the polymeric blend of PSf/PAN ES NF substrates on the FO process and compared it with a house-made (PSf/PAN) TFC-FO membrane (Fig. 5d) [75]. The effect of various draw solutions on FO performance was also investigated. The fabricated blend of ES NF substrate demonstrated improved porosity and tensile properties compared to the house-made blend of PSf/PAN support. The reduction in ICP was revealed by the higher FO performance of the nanofiber-based TFC-FO (NTFC) membrane. Fig. S3c shows the water fluxes of both TFC-FO membranes as a function of various DS solutions. The prepared NTFC membrane exhibited a remarkable

enhancement in water flux compared to the TFC-FO membrane, demonstrating the feasibility of using blended ESNF substrates in the fabrication of TFC-FO membranes [75]. Using the same approach, our group used a polymer blend of PES/PAN ESNF substrate for the fabrication of the NTFC-FO membrane [27]. In this work, the impact of the PAN content on the hydrophilicity, water uptake, and roughness of the ESNF blend was also investigated. From the SEM cross-sectional image

of the pristine PES ESNF (Fig. 5e) and the blend PES/PAN ESNF (Fig. 5f) supports, it was noticed that the sizes of the interconnected pores in both substrates are in the same range of 10–200 nm, indicating that the addition of hydrophilic PAN to the pristine ESNF support improved the wettability without sacrificing the porosity within the nanofiber. The best optimized NTFC-10 membrane (prepared with a 90:10 PES/PAN blend ratio) achieved a water flux of 42.1 and 52.2 LMHs, and a specific

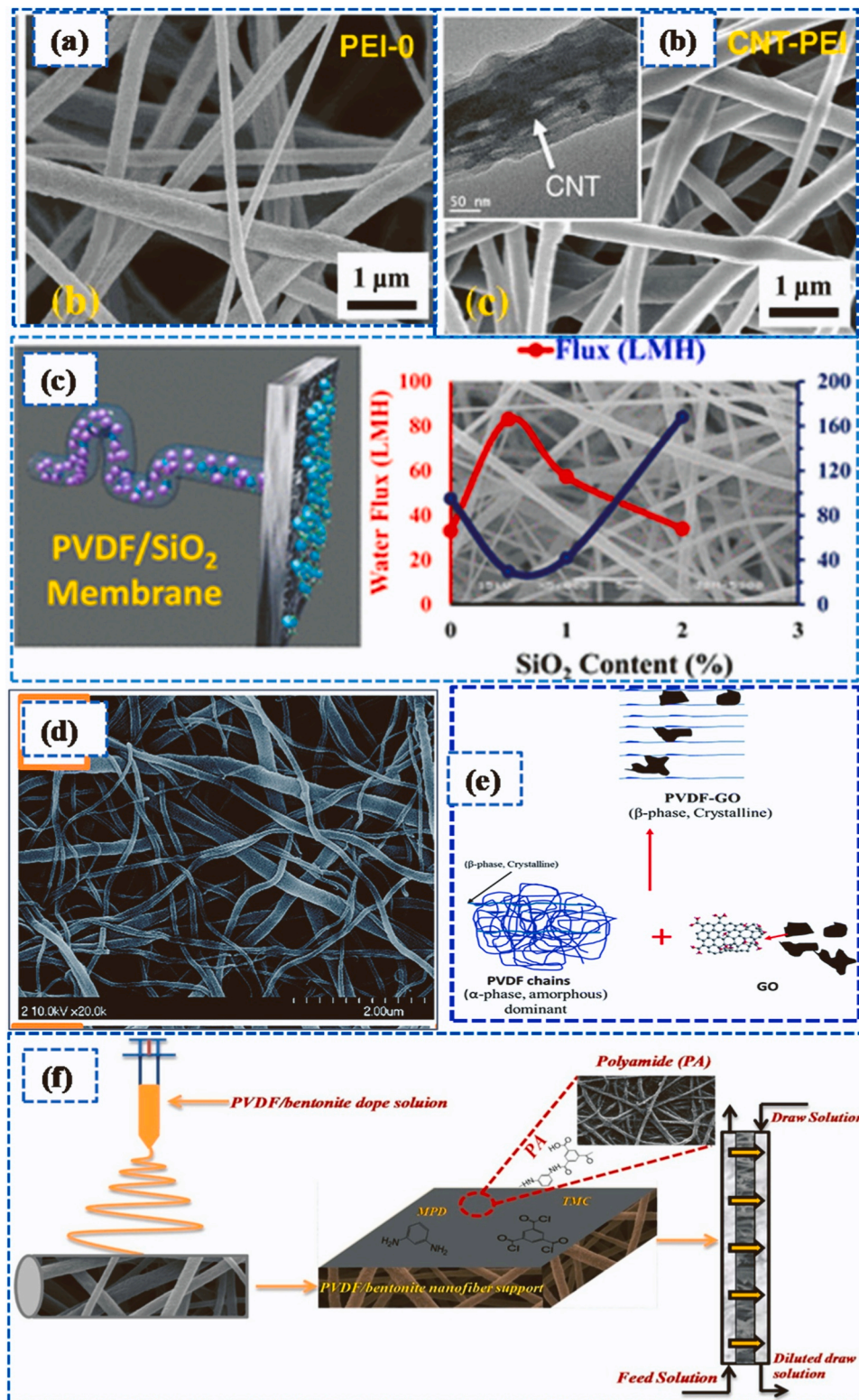


Fig. 6. (a-b) SEM image of the pristine PEI ESNF and CNT-PEI ESNF substrates ‘reproduced with permission from Tian et al. [84]’. (c) TFC membranes incorporated with PVDF-ESNF based on amorphous silica nanoparticles for high flux FO desalination ‘reproduced with permission from Obaid et al. [56]’. (d) FE-SEM images of the developed free-standing PVDF-GO ESNF substrate, (e) the interaction mechanism between GO and PVDF and the formation of the b-phase ‘reproduced with permission from Obaid et al. [58]’. (f) Bentonite nanoclay incorporated ESNF-based TFC-FO membrane fabrication process ‘reproduced with permission from Shah et al. [71]’.

salt flux of 0.27 and 0.24 g/L for the FO and PRO modes, respectively (see Fig. 5g).

4. Nanocomposite ESNF substrates and nanoparticle-incorporated ESNF

As nanotechnology and material chemistry research activities merge, an advanced process has been established to develop high-performance membranes by incorporating nanoparticles (NPs) into polymeric substrates known as nanocomposite membrane substrates [21,28,72]. Incorporating a small amount of NPs in the membrane substrate improves hydrophilicity, reduces the structural parameter, and improves the mechanical strength of the substrate [15,33,62]. Different types of NPs, such as SiO₂, TiO₂, Al₂O₃, carbon nanotubes (CNTs), zeolite, polydopamine (PDA), and graphene oxide (GO), have been introduced to modify the substrate of the TFC membrane [13,14,66].

A high-performance nanocomposite TFC-FO membrane (TFN-FO) was developed using a polyetherimide (PEI) ESNF substrate reinforced by functionalized CNT (f-CNT) along with a PA layer [84]. Fig. 6a and b displays the SEM image of the pristine PEI ESNF and CNT-PEI ESNF substrates, respectively. The TEM image of CNT-PEI (inset of CNT-PEI SEM image) confirms the successful incorporation of CNTs into the ESNF substrate. Incorporating f-CNT into the ESNF substrate reduced the structural parameter (S) value by 30% and increased the tensile modulus by 53%. As can be seen from Fig. S4a, the best nanocomposite TFN-FO (TFN-2) membrane showed a water flux of 61 LMH (AL-DS orientation) with a low specific solute flux and a structural parameter of 310 μm [84]. Obaid et al. developed TFC membranes incorporated with PVDF-ESNF-based amorphous silica nanoparticles for high-flux FO desalination (Fig. 6c). In this work, silica NPs were extracted from rice husks and introduced to the ESNF substrate. The FO membrane with 0.5 wt% NPs showed a salt rejection of 99.7% and water flux of 83 LMH, with the lowest structural parameter of $S = 29.7 \mu\text{m}$ [56].

The potential for commercialization of ESNF-based TFC-FO membranes is low in doubt, and exploring the entire parameters for the fabrication of ESNF-based substrates is increasing in importance. Bui et al. [49] reported a scalable approach to preparing ESNF-based FO membranes with high performance. In this work, mesoporous silica nanoparticles were incorporated into PAN nanofibers during electrospinning. The FO membrane with the composite ESNF substrate achieved a 2 times enhanced water flux performance in both FO and PRO orientations compared to the bare FO membrane [5]. The increased water flux performance was expected to enhance the wettability of the support layer. The resulting membrane exhibits a low specific salt flux of ~75–85% lower than the commercial HTI membrane. Due to the high hydrophilicity and chemical stability of TiO₂, it is being used to enhance membrane separation performance. Zhang et al. improved the water flux of the FO membrane by 19% using PSf/TiO₂ ESNF as substrate material compared to the controlled TFC membrane [96], indicating a potential ESNF substrate for FO membrane fabrication. Among inorganic NPs, GO has attracted much attention in the preparation of nanocomposite membranes for wastewater treatment applications due to its chemical stability, high surface area, chemical tunability, and excellent hydrophilicity [22,63]. Recent times have seen a huge development in research related to free-standing membranes for several applications, including TFC membranes for the FO process. A highly permeable novel high-performance TFN-FO membrane was developed using a graphene oxide (GO, ranging from 0.1 to 15 wt%) incorporated PVDF freestanding robust nanofiber substrates (Fig. 6d) in Obaid et al., work [58]. The interaction mechanism between GO and PVDF and the formation of the b-phase can be seen in Fig. 6e. The developed ESNF-based TFC membrane prepared using this approach achieved the lowest structural parameter of 85.5 mm, indicating a significant reduction in the ICP effect. The results also showed improved water permeability, which is approximately 167% higher than the standard TFC-FO membrane (Fig. S4b).

There are two major issues with PA formation on ESNF-based substrates: 1. PA layer defect due to the ESNF substrate's large pore size and 2. Difficulty in handling the ESNF mat in the IP process due to its flexibility. Due to its excellent properties, such as hydrophilicity, environmentally friendly, inexpensive, and chemical stability, bentonite nanoclay has attracted more attention with abundant availability compared to other NPs, such as CNT, GO, etc. To overcome the issue with the PA layer in the IP process with the ESNF substrate, bentonite nanoclay has been used as a nanofiller to fabricate the ESNF-based TFC-FO membrane (see Fig. 6f) [71]. Furthermore, due to the incorporation of the bentonite nanoclay, the hydrophobic PVDF imparts the β polar phase and reduces the α non-polar phase [71]. As shown in Fig. S4c, the developed TFN FO membrane with the highest bentonite content (2.0 wt %) exhibited a water flux of 40.64 LMH with a reverse salt flux of 4.23 g/m² h (gMH) without a considerable enhancement in reverse salt flux (RSF), indicating the formation of a defect-free PA layer on the composite ESNF substrate (see inset in Fig. S4c). Although membrane substrates for TFC-FO membrane fabrication have many benefits, biofouling is a major concern [53]. To overcome this problem, antimicrobial NPs such as GO, Ag, TiO₂, etc. have been incorporated into the ESNF-based substrates to enhance the anti-biofouling properties. Among several antimicrobial NPs, Ag NPs are promising agents due to their excellent hydrophilicity and antimicrobial activity [45].

Pan et al. developed an antibacterial PAN ESNF mat decorated with Ag particles synthesized in situ for a nanocomposite TFC-FO (TFN-FO) membrane (Fig. 7a) [61]. As can be seen from Fig. 7b and c, compared to cells attached to the pristine ESNF substrates (NFS), cells on composite Ag/PAN substrate showed 'pits', indicating the biotoxicity of the incorporated Ag NPs. The resulting Ag/PAN-TFN FO membrane exhibited excellent antibacterial activity against *E. coli* (96%) and *S. aureus* (92%) (Fig. S5a). Thus, this work suggests that the Ag NPs incorporated PAN ESNF substrate could be used as a potential support for the anti-biofouling TFC-FO membrane. In the field of sewage treatment for the removal of antibiotic resistance genes (ARGs), TFC-FO membranes suffer from biofouling that affects separation performance. A novel ESNF-based TFC-FO membrane has been designed for applications in antibacterial activity [9]. In this work, Ag-doped TiO₂ NPs (TiO₂/Ag) were incorporated into PSf ESNF substrates used to fabricate a TFC-FO membrane to remove tetracycline-resistant genes (TRGs). Fig. 7d shows the antimicrobial mechanism of the TiO₂/AgNPs modified FO membrane. Fig. 7e-f shows the SEM images of the pristine ESNF FO and the TiO₂/Ag NPs modified FO membranes with *E. coli* cells on the membrane surface. Cells attached to the composite FO membrane can be seen to have structural damage (cracks and pits, Fig. 7f), due to the presence of TiO₂/Ag NPs. Doping with TiO₂/Ag NPs enhanced the water flux to 56.49 LMHs in the PRO mode. The composite FO membrane exhibited strong fouling resistance and bacterial inhibition (65% of *E. coli*, Fig. S5b) and effectively rejected tetracycline-resistant bacteria (TRB) and TRGs.

In addition to ICP in the FO process, the structural stability of TFC-FO membranes is also a major concern that affects separation performance. According to the reported studies, structural stability can be improved by introducing adhesive NPs with reactive functional groups [92,93]. The adhesion strength of the membrane substrate could be improved by introducing reactive functional groups, which could participate in the IP process on the membrane substrate surface. Polydopamine (PDA) NPs have received considerable research attention due to their strong adhesiveness and abundant reactable functional groups (catechol and amino moieties) [30]. To reduce the ICP in the FO process and improve the structural stability of the TFC-FO membrane, Luo et al. designed a TFC-FO membrane based on a reactable hydrophilic ESNF substrate. In this work, an ESNF composite reactable substrate was successfully fabricated by vacuum filtering an interlayer composed of PDA NPs onto a PAN ESNF substrate (see Fig. 7g) [47]. According to the T-peel test, the designed TFC-FO membrane exhibited enhanced adhesion strength between the PA layer and the ESNF substrate due to the chemical bonding

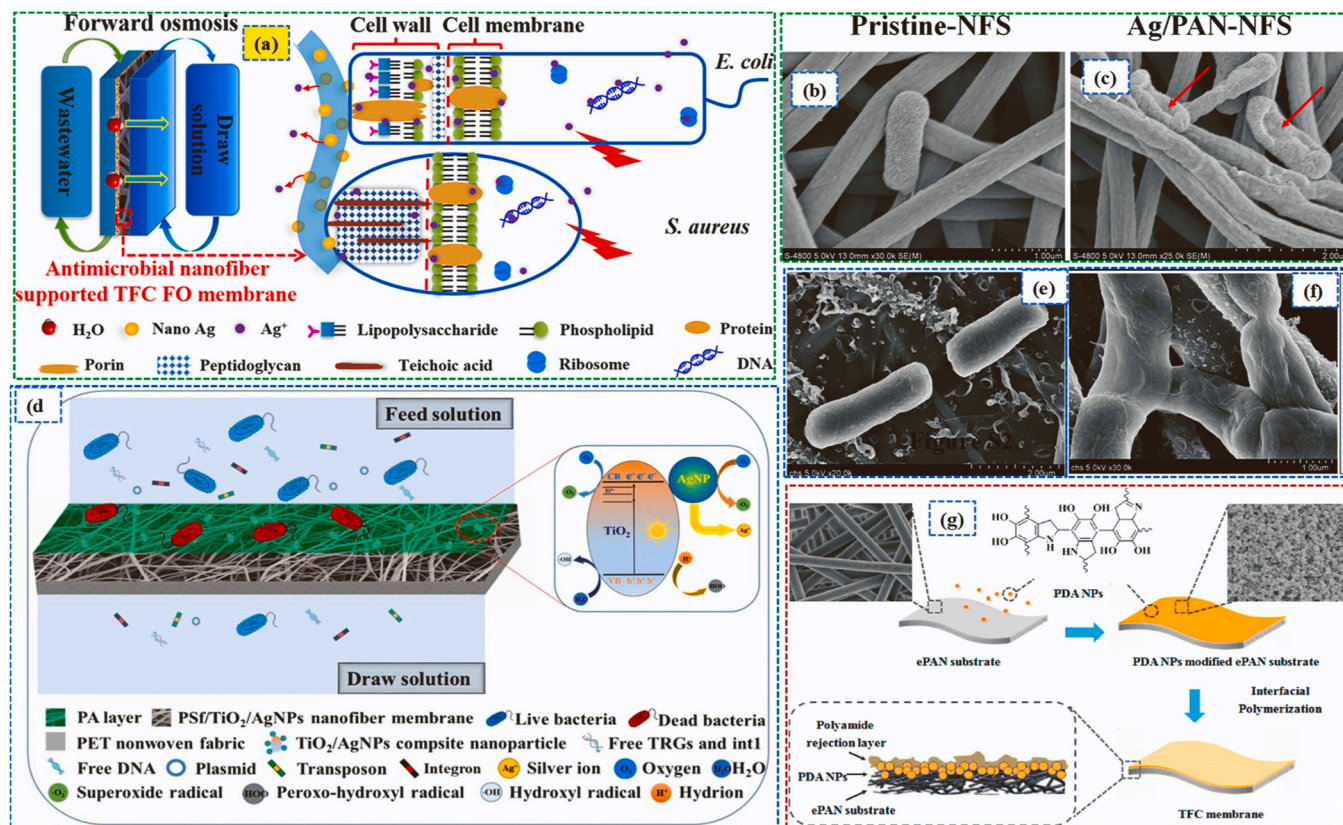


Fig. 7. (a) Schematic representation of antibacterial PAN ESNF-Ag NPs for the TFC-FO nanocomposite membrane, (b-c) SEM images with the attachment of the bacterial cell 'reproduced with permission from Pan et al. [61]. (d) Schematic representation of the antimicrobial mechanism of TiO₂/AgNPs modified FO membrane, (e-f) SEM images of the pristine ESNF FO and the TiO₂/Ag NPs modified FO membranes with *E. coli* cells on the membrane surface 'reproduced with permission from Chen et al. [9]. (g). Schematic representation of PDA nanoparticles modified ESNF-based TFC-FO membrane substrate 'reproduced with permission from Luo et al. [47]'.

and strong adhesion between ESNF and the PDA NPs. The TFC-FO membrane showed 1–2 times enhanced water flux (29.2 ± 0.3 LMH) compared to HTI-TFC, and a high removal rate for Cr³⁺ (99.5%), Cu²⁺ (99.1%) and Ni²⁺ (98.1%) (Fig. S5c). The results indicate a pathway for the design of nanofiber-based FO membrane with modified structure stability and high performance by IP process.

5. Surface modification

Modification of the membrane surface is one of the extensively used methods for preventing ICP in the FO process. Different surface modification techniques have been reported, including coating, cross-linking, grafting, layer-by-layer (LBL) deposition, thermal treatment, etc.

5.1. Coating and cross-linking

The coating is commonly used for surface alteration and is applied in the design of 2/3-tier composite membranes. In this process, a new layer of film is formed on the surface of the membrane substrate [95] [65]. Along with the blending process, the surface coating also plays an important role in reducing the ICP problem in the FO process. A (CaCO₃)-coated PES-based FO membrane substrate was developed by Liu et al. [42]. In this work, the hydrophilicity of the membrane substrate was increased, and the S parameter was reduced due to the intrinsic hydrophilicity of the CaCO₃ coating. For the fabrication of high-performance NTFC membranes, achieving a desirable minimum thickness of the barrier layer is crucial. You et al., group [95] developed a facile method to achieve an ultrathin hydrophilic layer on the ESNF support layer. In this work, high flux ESNF-based TFC ultrafiltration

membranes containing a hydrophilic PVA–multi-walled carbon nanotubes (MWCNT) nanocomposite barrier layer and a PAN ESNF substrate were fabricated, and a schematic illustration of the preparation method is shown in Fig. 8a. Inspired by this, a novel ESNF-based TFC-FO membrane has been designed using CNTs as an interlayer between the PAN ESNF substrate and the active layer of PA [91]. The cross-sectional SEM images of TFC-FO membranes with and without CNTs interlayer between the ESNF substrate and the PA active layer are shown in Fig. 8b and c, respectively. As shown in Fig. S5a, the incorporation of CNTs interlayer reduced the pore size of the ESNF substrate from 0.60 μm to 0.30 μm to provide a better surface for the PA layer formation, which prevents the transport of the draw solution. The developed FO membrane showed 83.55% higher water flux and 75.58% lower salt flux than the pristine FO membrane. As shown in Fig. S5b, the modified FO membrane is also highly selective (lower J_s/J_w values indicate lower leakage of the draw solute).

A low tortuous and high hydrophilic cross-linked PVA ESNF substrates were successfully fabricated [68]. In this work, ESNF substrates were chemically cross-linked using glutaraldehyde to provide a water-insoluble and mechanically stable composite ESNF substrate for the preparation of a low ICP TFC-FO membrane. The resulting TFC-FO membrane showed 7–8 times enhanced FO water flux compared to a commercially available FO membrane [68]. Furthermore, the FO membrane showed a lower structural parameter ($S = 66 \pm 7.9$), a measure of internal concentration polarization (ICP). Although hydrophilic ESNF-based TFC-FO membranes achieved high flux and low structural parameters due to fully wetted and interconnected pore structures, it has been reported that hydrophilic ESNF undergoes fiber swelling that decreases the strength of each fiber and junctions between

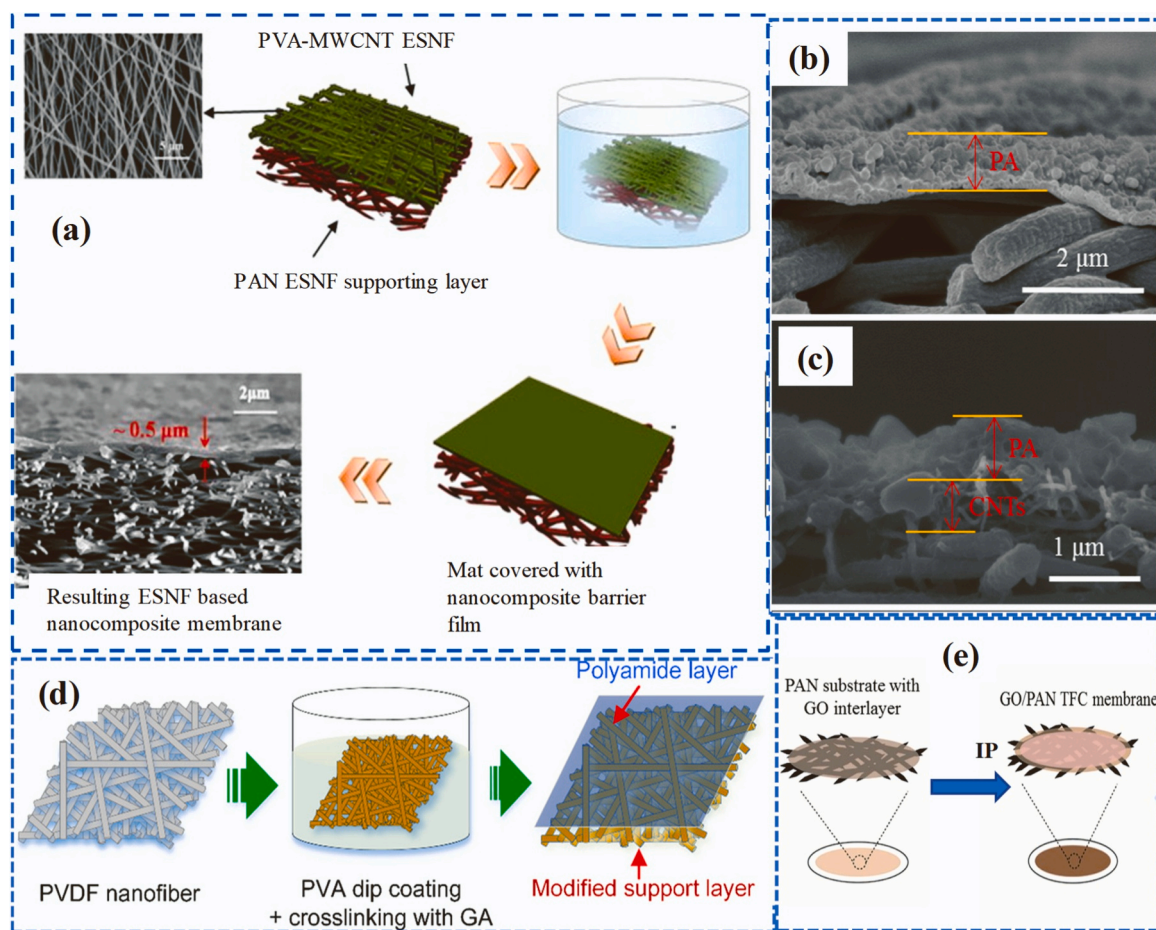


Fig. 8. (a) Schematic representation of the fabrication method for TFC membranes based on the PAN ESNF substrate and cross-linked PVA-MWNT barrier layer 'reproduced with permission from You et al. [95]. (b-c) Cross-sectional SEM morphologies of TFC-FO membrane with and without CNTs in ESNF support layer 'reproduced with permission from Yang et al. [91]. (d) Schematic illustrations of hydrophobic PVDF ESNF support modifications via PVA dip coating 'reproduced with permission from Park et al. [65]. (e) Schematic representation of TFC-FO membrane fabrication based on GO nanosheets filtered PAN ESNF substrate 'reproduced with permission from Wu et al. [88].

fibers [25]. To address this swelling problem, Huang et al. proposed using a hydrophobic fiber with a surface modified to be a hydrophilic material [24]. Such a hydrophobic ESNF substrate can display wetting properties without swelling issues due to the core hydrophobic polymer that resists swelling. Following this concept, hydrophobic PVDF nanofibers were successfully coated with hydrophilic nylon 6,6 [24]. In this work, the hydrophilic layer was directly formed on the hydrophobic PVDF ESNF substrate using the IP process of 1,6-hexane diamine and adipoyl chloride. The ATR-FTIR and SEM images from Fig. S6c-e confirm the successful coating of the 6,6 layer onto the PVDF ESNF substrate. This approach has resulted in the ESNF substrate with greatly improved wettability and mechanical properties, without altering the ESNF morphology. The resulting FO membranes showed significantly lower swelling propensity and excellent water flux with the lowest structural parameters [24]. In another study, a hydrophilic PVA dip coating was applied to a PVDF ESNF substrate to improve its hydrophilicity and tensile properties [65]. However, PVA is soluble in water. To overcome this shortcoming, the ESNF support was modified with PVA dip coating and acid-catalyzed cross-linking with glutaraldehyde before PA layer formation (Fig. 8d). The dip-coating and cross-linking approach reduced swelling in water and improved hydrophilicity without compromising the porosity of the ESNF substrate. This consequently reduced ICP effects, demonstrating enhancements in FO performance. Park et al. [65].

One of the main drawbacks of ESNF substrates for the preparation of TFC-FO membrane is their large pore sizes (micron-/submicron-scale)

that obstruct the formation of a PA layer with good integrity. Due to this drawback, some defects would be created in the active layer, leading to a direct pathway for salt transport and decreasing the solute's selectivity [26]. To overcome this problem, recent studies have reported that an intermediate layer is applied to the microporous substrate [99,100]. Recently, the pore size and roughness of the ESNF substrate have been adjusted by GO nanosheet and inhibited deep PA growth in the pores of PA into ESNF substrate pores [88]. In this work, the GO nanosheets were vacuum filtered on the surface of the PAN ESNF substrate (Fig. 8e). The modified FO membrane with appropriate loading of GO nanosheets exhibited an improved water flux of 32.7 LMH (see Fig. S6f) and a lower specific salt flux of 0.26 g/L, demonstrating GO nanosheets as the promising modifier of ESNF substrates.

5.2. Thermal treatment

Recently, thermally treated ESNF substrates have gained significant interest in FO applications [27,78,101]. Thermal-rolling pretreatment of ESNF substrates prevents the exfoliation of the nanofibers and maintains their integrity [27,29,78,101]. Additionally, this treatment delivers a denser structure and a network between the nanofibers that are beneficial for the creation of a packed surface for the deposition of the polyamide layer. Several works are using thermally treated substrates for TFC fabrication. Son et al. prepared continuous thermal-rolling treated ESNF substrates for better deposition of the PA layer on top of it [69]. It was found that the TFC membrane with the modified ESNF

substrate showed an exceptional combination of water flux (30 LMH) and specific salt flux (0.57 g/L) at the engineered osmosis platform. Recently, our group used thermally treated ESNF substrates for the TFC-FO membrane preparation [27,29]. In this study, PAN hydrophilized PVDF-based ESNF substrates were used to produce TFC-FO membranes. The thermal treatment procedure is shown in Fig. 9a. First, the blended ESNF substrates were fabricated using the electrospinning technique. Second, continuous thermal-rolling pretreatment was performed on the ESNF substrates by being squeezed between 2 rubber rollers at a temperature of 100 °C, before the deposition of the PA active layer by the IP process. Because of the improved interconnection between adjacent blend nanofibers, the thermally treated ESNF substrate exhibited tensile properties higher than those of the as-spun (non-thermally treated) ESNF substrates. The results showed that the thermally treated PVDF ESNF substrate exhibited the highest tensile

strength of 7.5 Mpa and an elongation of 28.0% (see Fig. 9b). Furthermore, the developed ESNF-based TFC-FO membrane exhibited 191% higher water flux, improved selectivity (0.23 g/L), and a lower S than the pristine TFC-FO membrane[29].

The above studies demonstrate that mechanical properties can be significantly improved via thermal treatment to meet the demand for FO operation. However, the fabrication of a defect-free PA layer on ESNF substrates remains a major challenge. To meet this demand, both hot-pressing and bio-inspired coating strategies were used to fabricate a novel ESNF-based TFC-FO membrane by the Meng et al. group [52]. In this study, before PA layer deposition by the IP process, the ESNF substrates were subjected to hot-pressing, followed by bio-inspired PDA deposition to prepare robust and hydrophilic ESNF substrates (Fig. 9c). The smooth, defect-free (see AFM images in Fig. 9d-e) and improved hydrophilicity of the modified TFC-FO membrane exhibited double

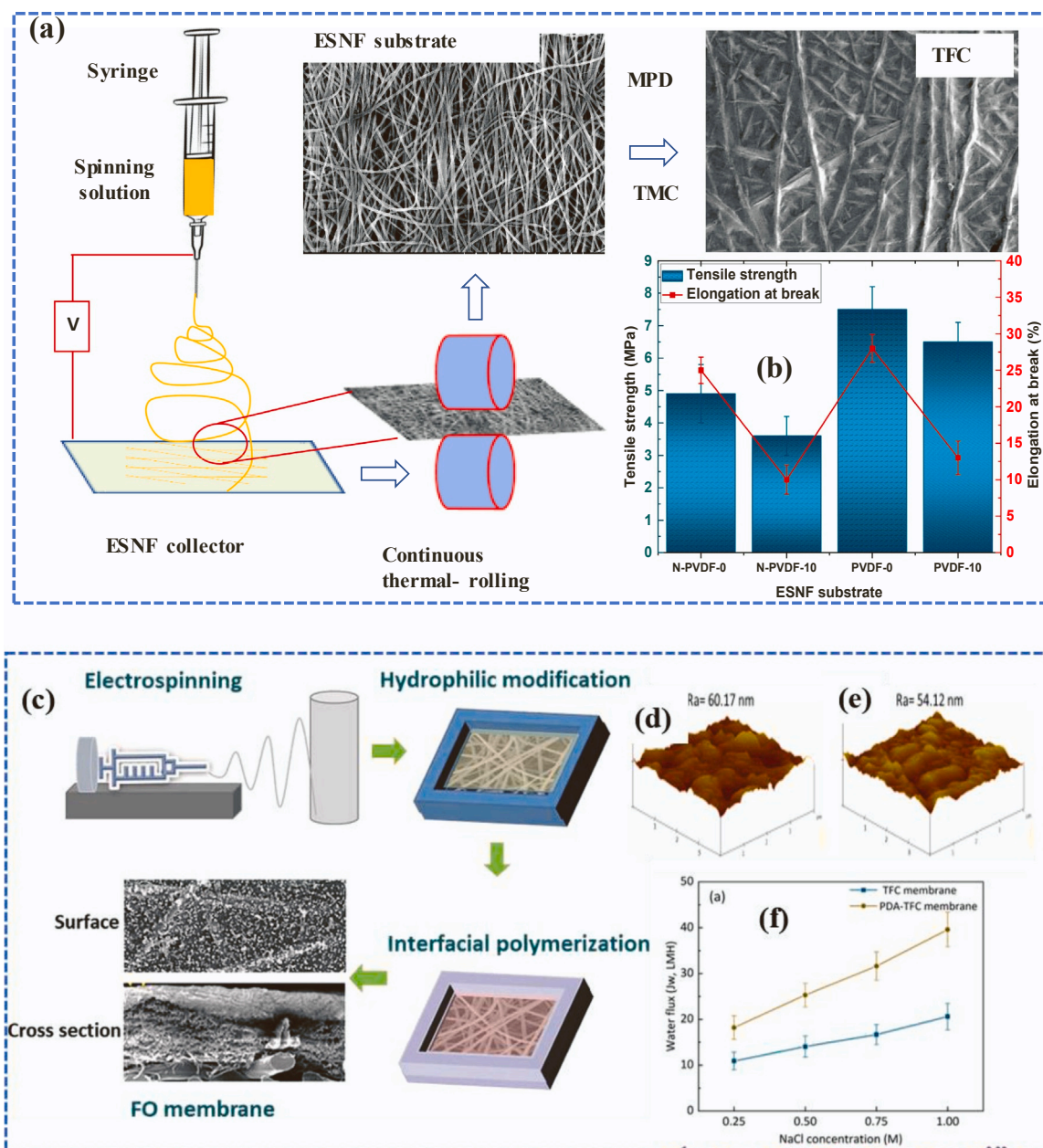


Fig. 9. (a) Procedure of continuous thermal-rolling pretreatment on PVDF/PAN ESNF substrate before PA later formation, (b) tensile properties of thermally treated ESNF substrate 'reproduced with permission from Kallem et al. [27,29]'. (c) TFC-FO membranes based on ESNF substrates with hot-pressing, followed by the deposition of bio-inspired PDA. AFM images (d-e) and FO water flux (f) result from a pristine and modified TFC-FO membrane 'reproduced with permission from Meng et al. [52]'

water flux compared to the pristine TFC-FO membrane (Fig. 9f). The PDA-TFC FO membrane displayed relatively high rejections (97.9–100%) for all heavy metal ions and antibiotics in model wastewater with good anti-fouling properties [52].

5.3. Other advanced approaches

5.3.1. Aligned nanofibers

Aligned ESNF-based membranes have recently been used as thin-layer chromatographic media and proton exchange membranes. They feature unique slit-like pore structures created by gaps between parallel and well-aligned nanofibers [17,34,85]. Furthermore, it has been reported that membranes with unified slit-shape pores exhibited 10–100 times higher water flux than commercial membranes due to their larger pore size and better pore interconnectivity [18]. For the first time, well-aligned ESNF substrates with slit-shape pore structures were successfully fabricated and used to design the high-performance TFC-FO membranes (Fig. 10a) [19]. Fig. 10b–c display two types of ESNF arrangements, random and aligned. In this work, a PAN-based ESNF substrate was prepared at various rotating speeds (500–2000 rpm) and then hot-pressed to achieve a smooth surface for PA layer formation. The resulting TFC-FO membrane fabricated from an aligned ESNF substrate with slit-shape pores showed a thinner PA than the TFC-FO membrane prepared from a randomly oriented ESNF substrate, and therefore high water fluxes of 50.7 and 62.9 LMH in the FO and PRO modes (Fig. S7a),

respectively, with low specific salt flux, demonstrating a mitigated ICP effect.

5.3.2. Dual-layered ENSF substrate via coaxial electrospinning

A new type of ESNF substrate was fabricated via coaxial electrospinning to improve TFC-FO membrane performance [74]. In this work, a dual-layered ESNF substrate was fabricated using mechanically strong PVDF and hydrophilic CA for the core and sheath sides, respectively (Fig. 10d). The coaxially based CA/PVDF ESNF-based TFC membrane exhibited a competitive water flux of 31.2 LMH and a lower specific salt flux of 0.03 g/L compared to the pristine and blend-based TFC membranes (Fig. S7b). Therefore, coaxial electrospinning is a promising and efficient method to improve the performance of the TFC FO membranes.

5.3.3. Sublayer binding into ESNF

Although ESNF-based TFC-FO membranes possess relatively low structural parameters and excellent permeability, there are still some drawbacks to ESNF-based TFC membranes, such as easy deformation and weak interfacial strength between the substrate layer and the PA layer. A novel composite substrate layer was designed as the support layer to overcome these problems by introducing a sub-layer on the ESNF mat [73]. In this study, the chitosan sub-layer was used to improve the mechanical strength between the PAN-based ESNF substrate and the PA layer. The schematic diagram of the composite TFC-FO membrane preparation is shown in Fig. 10e. The developed composite TFC-FO

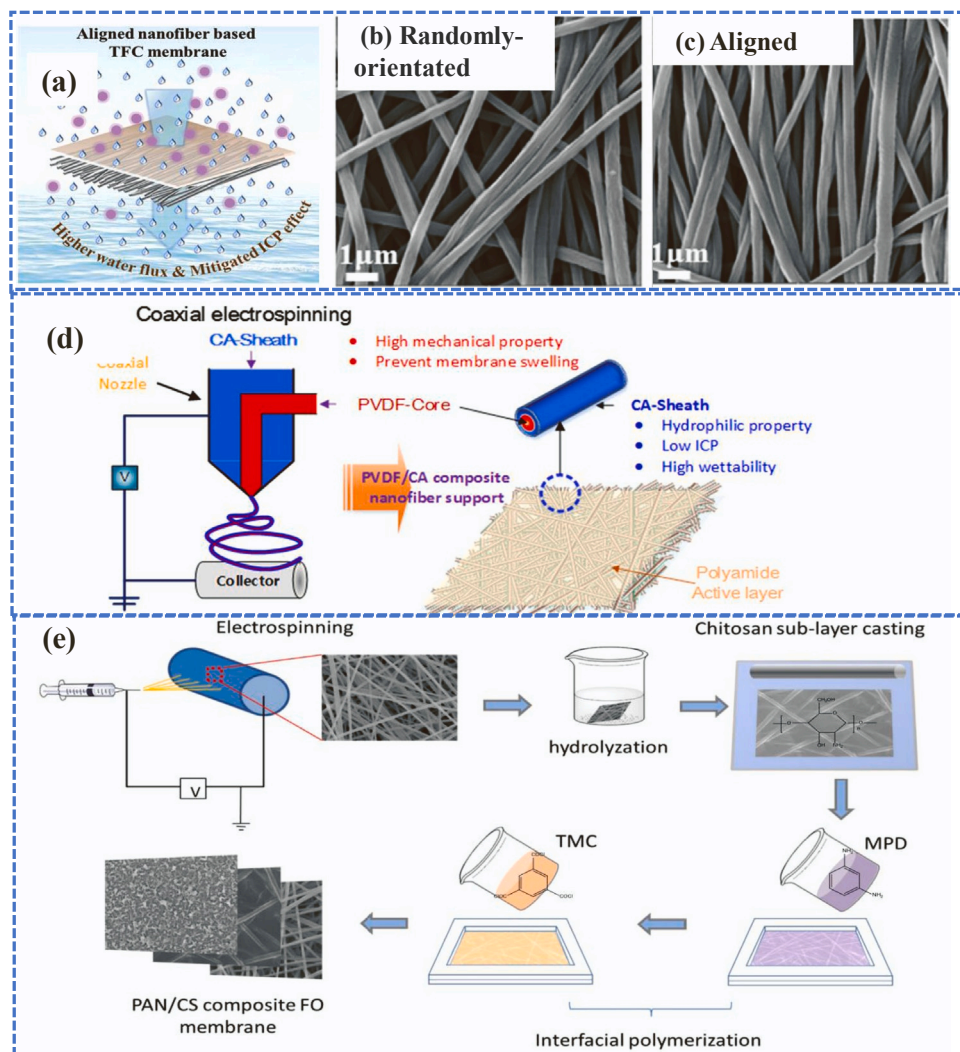


Fig. 10. (a) Schematic representation of FO performance using TFC-FO supported by well-aligned ESNF substrates with slit-shape pore structures. FE-SEM images of randomly (b) and aligned (c) oriented ESNF substrates 'reproduced with permission from Han et al. [19]'. (d) Dual-layered CA/PVDF ENSF substrate preparation method via coaxial electrospinning 'reproduced with permission from Shibuya et al. [74]'. (e) The schematic diagram of the preparation of a composite TFC-FO membrane based on the ESNF layer in which a sub-layer was introduced 'was reproduced with permission from Shi et al. [73]'.

membrane exhibited improved mechanical properties (Young's modulus of 90 MPa and tensile strength of 30 MPa) and higher water flux (over 60 LMH). Furthermore, the composite membrane showed a low reverse salt of 0.93 gMH and a lower structural parameter (203 μm only), which is significant to break the bottleneck in FO [73].

5.3.4. LbL polyelectrolyte deposition

Based on the combination of various polyelectrolyte pairs and substrates, the LbL assembled membranes have been extensively used for many applications, including wastewater treatment, due to their

advantages, such as ease of film formation and film stability [41]. The LbL technique has recently been applied to prepare FO membranes [11, 40, 94]. Until now, there has been very limited research on LbL-based ESNF membranes for TFC-FO applications. Gonzales et al. developed an LbL-based ESNF substrate to fabricate TFC-FO membranes [16]. In this work, polyacrylic acid (PAA) nanofibers were deposited on a prepared PVDF ESNF mat to form a PVDF-PAA substrate layer, followed by an LbL deposition of polyethyleneimine (PEI) and PAA to form a polyelectrolyte layer on the ESNF surface before PA layer formation. Results show that the PVDF-LbL TFC membrane showed superior performance

Table 1
FO performance of ESNF-based TFC-FO membranes fabricated by different methods.

Material for ESNF-TFC	Approach	Applications	Results	Limitations	Reference
PSf-PET	Single polymeric ESNF support	Engineered osmosis	Water flux (LMH) = 26.0, salt flux ($\text{g}/\text{m}^2 \text{ h}$) = 2.26×10^{-3}	Low hydrophilicity and lower mechanical strength. The poor interfacial adhesion between the ESNF layer and the PA layer	Bui et al. [3]
PES	scaffold-like single polymeric ESNF	Rejection of pollutants and salt ions	Water flux in FO mode (LMH) = 37.8 Salt rejection = 97%	Low flux. Durability and ICP	Song et al. [79]
PAN/CA	Blend polymeric ESNF	Water production, sustainable energy, and resource recovery	pure water permeability = 1.169 LMH/bar Salt permeability = 2.252 LMH	Limited Mechanical stability due to the brittle nature of CA. Low water flux.	Bui, McCutcheon [4]
ePET/PSf	Blend polymeric ESNF	Rejection of salt ions	pure water permeability = 1.13 LMH/bar Salt permeability = 0.23 LMH	Susceptibility to fouling and ICP	Hoover et al., [23]
PVDF	Single polymeric ESNF	Rejection of salt ions	Water flux (LMH) = 30.4, salt flux (g/l) = 0.21	Limited hydrophilicity and potential for fouling.	Tian et al., [83]
nylon 6, 6	Single polymeric ESNF	Rejection of salt ions	Water flux (LMH) PRO mode = 27, salt flux (g/l) = 0.44	Structural defects, durability, and low porosity	Huang, McCutcheon [25]
PET/PVA	Blend polymeric ESNF	Rejection of salt ions	Water flux (47.2 LMH), salt leakage (9.5 gMH)	Weak intermolecular forces between the two polymers and lower separation efficiency. Low selectivity	Tian et al., [82]
PVDF-SiO ₂	Nanocomposite ESNF substrates	Desalination	salt rejection = 99.7%, water flux = 83 LMH S = 29.7 μm	Increasing SiO ₂ to 5 wt% showed a negative impact on salt rejection. Enhanced porosity.	Obaid et al., [57]
PES	Thermally treated ESNF substrates	Engineered osmosis	Water flux (LMH) = 30.00, Reverse salt flux (gMH) = 17.00	Optimizing the process parameters and understanding the underlying mechanisms for PA deposition still require further investigation.	Son et al., [78]
PVDF-GO	Nanocomposite ESNF substrates	Rejection of salt ions	Water flux (LMH) = 54.6, salt flux (g L^{-1}) = 0.42	Factors such as fouling, scaling, and long-term durability are not fully evaluated.	Obaid et al., [58]
PAN/PSf	Blend polymeric ESNF	Rejection of salt ions	S (μm) = 34, Water flux (LMH) = 38.3, salt flux (g L^{-1}) = 0.27	This study does not provide information on the impact of ICP and S parameters on FO performance	Shokrollahzadeh, Tajik [75]
PVDF-PVA	Coating and cross-linking	Salt removal	S (μm) = 154, Water flux (LMH) = 24.8, salt flux (g L^{-1}) = 0.13	Hydrophilic coating on the ESNF is susceptible to degradation or fouling, which could impact its long-term performance. Structural and mechanical properties were not provided.	Park et al., [65]
CA/PVDF	Dual-layered ESNF via coaxial electrospinning	Salt removal	S (μm) = 190, Water flux (LMH) = 31.3, salt flux (g L^{-1}) = 0.03	Compatibility, adhesion, and mechanical stability	Shibuya et al., [74]
Chitosan-PAN	Sublayer incorporated ESNF	Rejection of salt ions	S (μm) = 203, Water flux (LMH) = 64.88 (PRO), salt flux ($\text{g}/\text{m}^2 \text{ h}$) = 0.93	Higher S value. Inter layer adhesion.	Shi et al., [73]
p-aramid nanofibers	Single polymeric ESNF	Rejection of salt ions	Water flux (LMH) = 19.9, salt rejection (%) = 98.6	Lower water flux. The dense and compact structure of p-aramid nanofibers.	Miao et al., [54]
TiO ₂ /Ag-PSf	Nanocomposite ESNF substrates	Removal of tetracycline-resistant genes	Water flux (LMH) = 56.49, permeability of tetracycline-resistant bacteria (TRB) (%) = 0.75	Optimization of TiO ₂ /Ag particles in the ESNF substrate to maintain stability. Cost and scalability.	Chen et al., [8]
PSf	Thermal treatment followed by PDA deposition	Rejection of heavy metal ions and antibiotics	S (μm) = 166, Water flux (LMH) = ~40, Rejection of Zn ²⁺ , Fe ³⁺ , and Cr ⁶⁺ (%) = 100, Rejection of TC (99.7%), SMZ (97.9%), and TMP (99.5%)	The stability of PDA. The PDA deposition process is a time-consuming and labor-intensive process, which can limit the scalability of the technology.	Meng et al., [52]
PES/PAN	Blend polymeric ESNF	Rejection of salt ions	Water flux (LMH) = 42.1, salt flux (g L^{-1}) = 0.27	Lack of long-term performance data	Kallem et al., [27]
PAN	Aligned	Rejection of salt ions	S (μm) = 86.4, Water flux (LMH) = 62.9 (PRO), salt flux (g L^{-1}) = 0.13	Limited comparison with existing FO membranes Tendency to suffer from structural defects due to the alignment process. Reduced water flux rates due to the limited number of pores and small pore size.	Han et al., [19]

in terms of improved hydrophilicity and porosity without compromising mechanical stability and robustness. Due to the effectiveness of the polyelectrolyte deposition, the permeability of pure water and the low structural parameters improved, achieving a value of 4.12 LMH/bar and 221 μm , respectively. These values are better than the conventional forward osmosis membrane. The developed PVDF-LbL TFC membrane displayed improved hydrophilicity and porosity without losing mechanical strength. As shown in Fig. S7c-e, the PVDF-LbL TFC membrane outperformed the commercial FO membrane [16]. Additionally, the resulting TFC-FO membrane exhibited a low structural parameter of 221 μm . Thus, the deposition of LbL is a feasible approach for improving FO membrane performance. Table 1 shows the progress in FO performance using ESNF-based TFC membranes fabricated by different methods.

6. Challenges

From the above discussions, FO technology has great potential for water purification applications; however, it has not been commercialized on a large scale due to the lack of a specific membrane structure for FO separation technology [73]. Although various membrane development technologies for ESNF-based TFC FO membranes for water and wastewater treatment have been discussed, certain challenges and problems need to be solved. Some prominent challenges related to developing ESNF membrane substrates are ICP, fouling, lack of mechanical strength, etc. The following challenges and drawbacks can be concluded from this review article:

- ICP is a major problem as it causes a decline in membrane efficiency, raises operating costs and reduces the stability of FO membranes. In addition to ICP in the FO process, the structural stability of TFC-FO membranes is also a major concern that affects separation performance.
- One of the crucial issues observed in the development of TFC membranes for the FO process is the problem of membrane fouling. Foulant materials originate from pollutants such as organic and inorganic materials, colloidal components, and microorganisms present in wastewater. The effects of fouling, such as biofouling, are associated with the formation of biofilms from microorganisms such as bacteria on the membrane surface. The formation of biofilms increases the resistance to mass transfer, ultimately leading to a decrease in flux. In addition, fouling has several adverse effects on the selectivity and lifetime of the TFC-FO membrane.
- Another important issue with the ESNF substrate is its poor mechanical strength as a result of the weak/poor connection between the fibers and its highly porous structure. The lack of mechanical strength of nanofibers restricts their adaptability in practical operation. This problem harms the filtration process since water purification applications require a mechanically stable substrate to resist dynamic operating conditions.
- In addition to these challenges, it is difficult to adopt nanofibers for water purification because of the defect-prone nature of the ESNF mats. When the nanofiber-based membrane is subjected to high pressure, there is a chance that the fibers can be easily delaminated, which makes them unfit for the filtration process. Another drawback with ESNF substrates for the preparation of TFC-FO membranes is their large pore sizes (micron-/submicron-scale) that obstruct the formation of a PA layer with good integrity. Because of this drawback, some defects would be created in the PA active layer, leading to a direct pathway for salt transport and diminishing the solute selectivity.
- Although the hydrophilic ESNF-based TFC-FO membranes achieved high flux and low structural parameters because of the fully wetted and interconnected pore structures, it has been reported that hydrophilic ESNF undergoes fiber swelling which decreases the strength of each fiber and junctions between fibers. The ESNF

substrates suffer from various complexities, such as wettability issues and poor adhesion between the support and active layers. Moreover, the fabrication of a defect-free PA layer on ESNF substrates remains a major challenge.

- As inferred from existing work, one of the potential drawbacks of ESNF membranes is the usage of toxic solvents. Although modern electrospinning techniques use iconic nonvolatile solvents for fabricating nanofibers, there is a lack of an effective electrospinning technique that can reduce the use of toxic solvents. These solvents are highly unstable, have a very low yield, and require a very high voltage for operation, which can be dangerous for the operators. These issues raise concerns about adopting the ESNF membrane substrates for TFC-FO membrane fabrication.

These issues must be effectively addressed to enhance the properties of ESNF-based membrane substrates for TFC-FO applications. Several challenges need to be resolved by inducing a collaborative effort in research related to ESNF-based FO membranes. These additional efforts can benefit water treatment industries, which can develop cost-effective and efficient ESNF-based FO membranes for desalination and water treatment.

7. Future recommendations

Next-generation sophisticated ESNF membrane substrates have established themselves as optimistic, assuring support with advanced features for water treatment. Modern ESNF membranes are considered potentially good candidates to treat wastewater effectively shortly. In the context of recent developments and state-of-the-art ESNF-based substrates, it can be inferred from existing work that ESNF-based TFC-FO membranes can be extremely promising and potentially stable for wastewater treatment and water filtration applications. When existing ESNF techniques are considered, the drawbacks can be resolved by combining the electrospinning technique with advanced nanotechnologies such as LBL, hybrid membranes, and cross-linking-based solutions, which can provide access to a variety of substrates with superior features. Based on their application in the water filtration process, ESNF membranes can be improved by increasing the fundamental understanding of different solvents, which can enhance the water permeability and membrane performance in terms of high aspect ratio and vast interconnected porosity. There is also a great need to expand the study related to enabling the scaling up of the ESNF membrane development technology for wastewater treatment.

Important parameters such as high porosity, low tortuosity, and low thickness are responsible for enhancing the water flux and controlling the intensity of ICP, fouling, and stability. The cross-linking approach can be applied extensively for the modification of ESNF substrates containing two or more polymer substrates. Cross-linking of two or more polymer substrates has gained huge significance in the design of membrane substrates. For the fabrication of the TFC-RO membrane, two types of acyl chloride-terminated hyperbranched polyesters (HBPAcs) with a three-dimensional structure were successfully synthesized by Wu et al. [87]. The synthesis process is shown in Fig. 11a. The HBPAc-based composite PA layer presented a certain cross-linking network, which maintained both the salt retention rate and improved compatibility of HBPAc in the PA main body. Importantly, rapid diffusion of water molecules through the PA layer of the membrane was achieved in RO applications (Fig. 11b) due to carboxyl groups from HBPAc that act as hydrophilic sites between PA chains. In another study, a composite membrane based on an integrally cross-linked polyimide-based (PI) composite membrane was developed by Li et al. [37]. The PI membrane was synthesized via interfacial polymerization (IP), followed by imidization, crosslinking, and solvent activation. During this process, different chemicals such as MPD, dopamine (DA), and benzene tetra-carboxylic acyl chloride (BTAC) were used along with an organic monomer (Fig. 11c). This approach has crosslinked the inner molecules

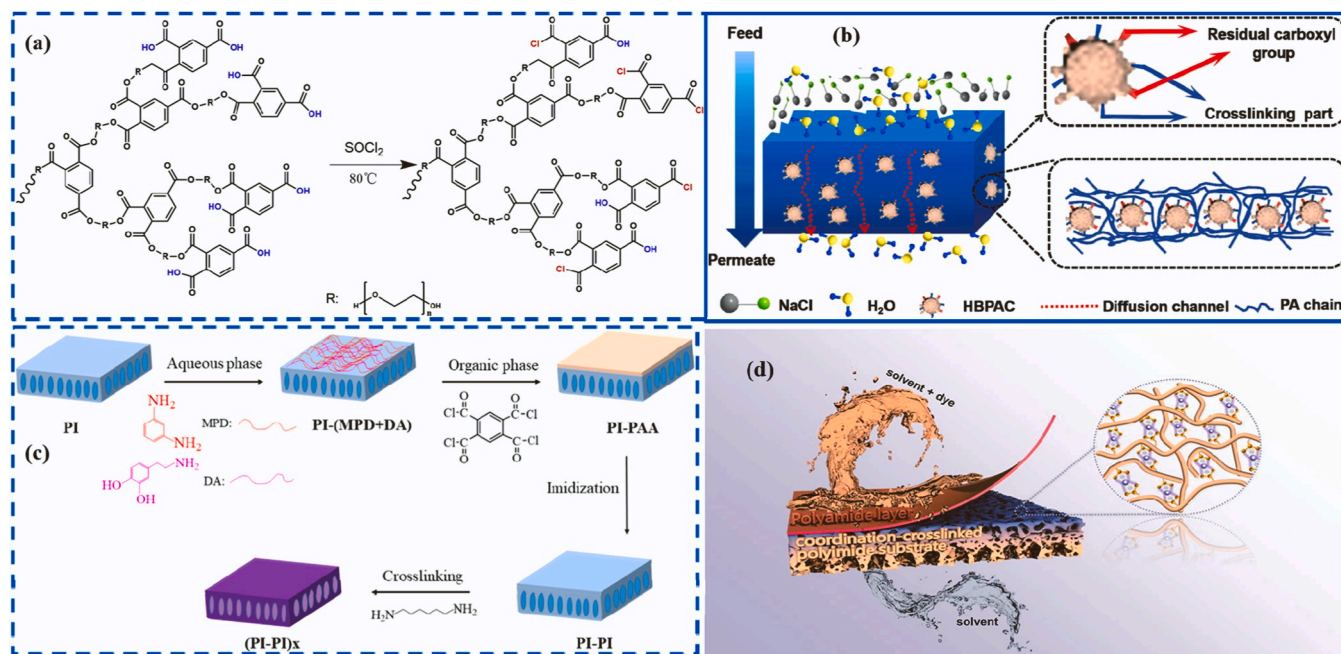


Fig. 11. (a) The one-pot synthesis process of HBPAC is based on HBP (a) and a schematic representation of the diffusion of water molecules through the PA layer of the cross-linked TFC membrane (b) ‘reproduced with permission from Wu et al. [87]’. (c) Schematic representation for the preparation of integrally cross-linked composite membranes ‘reproduced with permission from Li et al. [37]’. (d) Coordination-cross-linked polyimide supported membrane ‘reproduced with permission from Liu et al. [44]’.

of the membrane substrate, the inner molecules of the skin layer, and the interface molecules between the membrane substrate and skin, thus improving the membrane performance for NF applications. In the work reported (Fig. 11d), a novel coordination-crosslinked polyimide substrate was prepared [44]. In this work, a Ca^{2+} cross-linked PI substrate is fabricated and used to prepare the TFC membrane.

8. Conclusions

ESNF-based membrane supports are considered a promising class of materials for TFC-FO membrane supports due to their unique properties, such as high porosity with interconnected pore structures. This review article focuses on the recent developments in the fabrication of ESNF-based supports using different approaches to fabricate TFC-FO membranes. Compared to the single polymeric ESNF-based TFC-FO membranes, the modified ESNF-based TFC membranes showed improved permeability, selectivity, tensile strength, chemical stability, and anti-fouling properties. To further promote ESNF-based TFC-FO membranes in various water treatment applications, including desalination, heavy metal ion removal, and bacteria removal, some key challenges such as ICP, fouling, lack of mechanical strength, etc. need to be solved. It has been difficult to eliminate ICP, but a few findings have successfully reduced its effects by decreasing the structural parameters of the ESNF substrate. Therefore, it is expected that the interest in this process will continue using advanced nanotechnologies such as hybridization, surface modification, cross-linking, layer-by-layer deposition of polyelectrolytes, etc.

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.

Data Availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2023.110231](https://doi.org/10.1016/j.jece.2023.110231).

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