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Advanced thin-film nanocomposite membranes embedded with organic-based nanomaterials for water and organic solvent purification: A review

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Abstract

Due to the versatile structures and functionalities as well as good compatibility with polyamide (PA) matrix, organic nanomaterials are promising candidates as fascinating nanofillers in PA selective layer to improve separation efficiency of thin film nanocomposite (TFN) membranes, which consist of a nanomaterials-embedded PA layer and a porous support layer. This review specially focuses on the current development of organic nanomaterials based TFN membranes for various aqueous-/organic-based separation processes, as organic nanomaterials are effective in avoiding the non-selective defects caused by the poor interfacial compatibility between inorganic nanoadditives and PA matrix. The synthesis, modification and utilization of organic nanofillers for constructing state-of-the-art TFN membranes as well as the proposed transport mechanism are highlighted. Encouraging results have demonstrated that the embedded organic nanomaterials not only provide possibility in breaking the trade-off between membrane permeability and selectivity and improving antifouling performance, but also render membrane with attractive properties for targeted applications, such as antimicrobial performance and boron removal. Despite of the excellent properties imparted by functional organic nanomaterials, significant challenges still exist for in-depth study and scale-up of TFN membranes. Thus, this review also attempts to offer insights on future directions of advanced TFN membranes with organic-based nanomaterials.

Keywords: thin film nanocomposite, polyamide membrane, organic-based nanomaterials, desalination, solvent purification

Contents

Nomenclature		OSN	Organic solvent nanofiltration
		PA	Polyamide
ADNPs	Zwitterionic dopamine nanoparticles	PDA	Polydopamine
AEPPS	N-aminoethyl piperazine propane sulfonate	PDP	Polydopamine-piperazine
AQPs	Aquaporins	PEG	Poly(ethylene glycol)
C-CNCs	Carboxylated cellulose nanocrystals	PIP	Piperazine
CNCs	Cellulose nanocrystals	PLEPS	Pulsed low energy positron beam system
COFs	Covalent organic frameworks	PPD	p-Phenylenediamine
DA	Dodecyl aldehyde	PSS	Poly(sodium 4-styrenesulfonate)
EFP	Evaporation-controlled filler positioning	RO	Reverse osmosis
FO	Forward osmosis	SCA	Sulfocalix[4]arene
GO	Graphene oxide	SEM	Scanning electron microscopy
HZNCs	Hollow zwitterionic nanocapsules	STCAss	Sulfothiacalix[4]arene
IP	Interfacial polymerization	STXM	Scanning transmission X-ray microscopy
LBL	Layer-by-layer	TA	Tannic acid
MD	Molecular dynamics	TEM	Transmission electron microscopy
MMP	Metal-induced ordered microporous polymer	TFC	Thin film composite
MOFs	Metal organic frameworks	TFN	Thin film nanocomposite
MPD	m-Phenylenediamine	TMC	Trimesoylchloride
mZIF	Poly(sodium 4-styrenesulfonate) modified ZIF-8	TOCNs	6-Tetramethylpiperidine-1-oxyl-oxidized cellulose nanocrystals
NF	Nanofiltration	ZIF-8	Zeolitic imidazolate framework-8
NMPS	Amino-functional mesoporous polymer nanospheres	ZNGs	Zwitterionic nanogels
NPs	Nanoparticles	ZNGTFNMs	ZNGs-based TFN membranes
OSFO	Organic solvent forward osmosis	ZPNPs	Zwitterionic polyelectrolyte nanoparticles

1. Introduction

Separation processes play a significant role in modern industries, where they account for 40-70% of both capital and operational costs [1]. In addition, the amount of energy used for separating chemicals occupies 10-15% of the world’s total energy consumption [2]. Compared with traditional separation and purification processes (e.g., distillation, evaporation, adsorption, extraction and chromatography), membrane technology is much more energy-efficient [3, 4].

Meanwhile, it possesses distinct economy, environment, and safety benefits. Since 1960s, membrane technology has experienced rapid growth and has been gradually applied for industrial applications. In the context of addressing global water scarcity, membrane separation for water reuse and desalination has drawn tremendous attention and made great achievements in both scientific and industrial communities. Aimed at more efficiently separating and recovering solvent in chemical and pharmaceutical industrials, membrane-based organic solvent separation is a rapid growing paradigm technology. Although the related membrane science remains relatively unexplored, its development can be motivated by research progress in water purification [5].

In the field of liquid filtration, thin film composite (TFC) membranes, which were first developed by Cadotte in 1970s, are widely studied and industrially applied due to their easy processability and economic feasibility [6]. Typically, TFC membranes are produced via interfacial polymerization (IP) between an amine monomer (e.g., m-phenylenediamine (MPD) or piperazine (PIP) in aqueous phase) and an acyl chloride monomer (e.g., trimesoylchloride (TMC) in organic phase) at the water/organic interface to form an ultrathin polyamide (PA) selective layer atop a porous support on a non-woven fabric (Figure 1a) [7-9]. Research and commercial practice has indicated that MPD/TMC chemistry is the most used for constructing reverse osmosis membranes with fully aromatic polyamide network, while PIP/TMC chemistry is commonly applied to fabricate semi-aromatic polyamide nanofiltration membranes (Figure 1b) [10]. The PA selective layer which allows for the permeation of solvent molecules while rejecting solutes is essential in determining membrane separation efficiency. However, trade-off between membrane water permeability and selectivity exists: increasing water permeability generally leads to decreased salt rejection, and vice versa [11-13], which hinders the elevation of membrane performance.

Further improvement of membrane performance is a necessity to reduce energy consumption and operation costs as well as to meet the complex requirement of applications [14-16]. Motivated by the advancements in nanotechnology and nanofabrication, thin film nanocomposite (TFN) membranes have been developed to further improve membrane perm-selectivity and other properties. Generally, TFN membranes can be divided into three types according to the incorporation position of the nanomaterials [17]. The most common type of TFN membranes are those featured with nanomaterials integrated in PA rejection layers (shown in Figure 1a). Alternatively, nanomaterials can be added in the substrate to prepare TFC membranes with a nanocomposite substrate or deposited on the substrate prior to interfacial polymerization to form TFN membranes with an interlayer. In this review, we mainly focus on TFN membranes with functional nanomaterials embedded in PA layers by adding them in monomer solutions. Of note, TFN membranes can not only be applied in aqueous-based media, such as reverse osmosis (RO), forward osmosis (FO) and nanofiltration (NF) processes for seawater/brackish water desalination and contaminant removal [18-20], but also can be used for molecular separation and purification in organic solvents, such as organic solvent nanofiltration (OSN) and organic solvent forward osmosis (OSFO) processes [21-24]. In addition to liquid separation, TFN membranes also gain great attention and have been widely applied for gas and vapor separation [25-27].

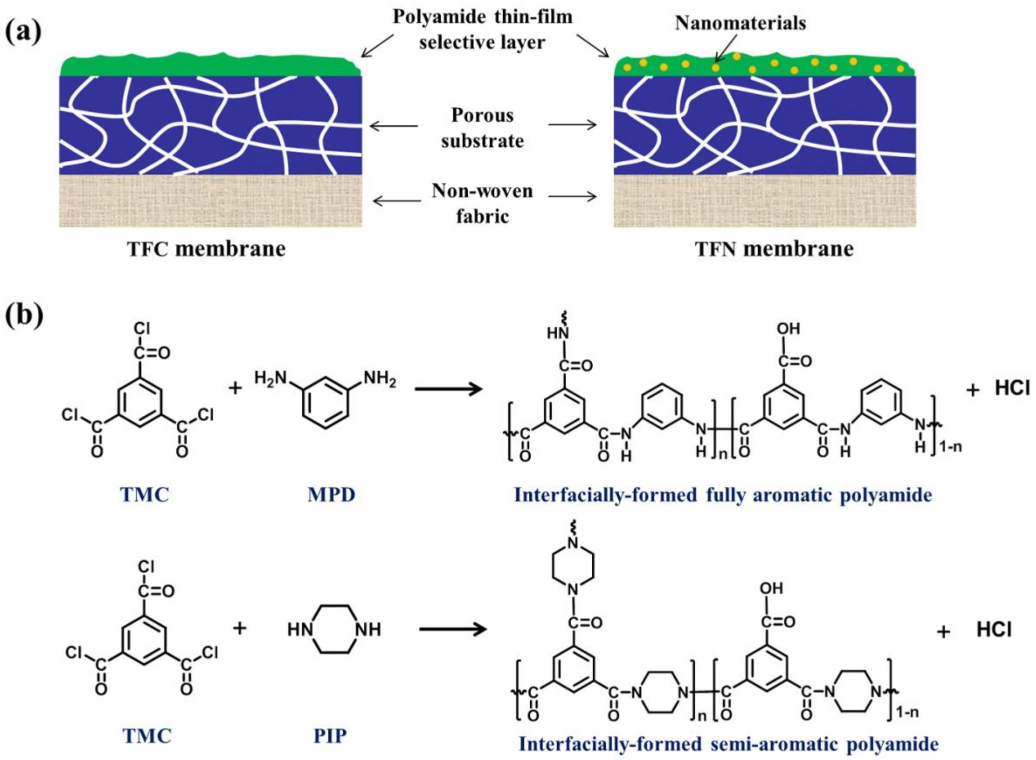

Fig. 1. Schematic diagram of (a) structures of TFC membrane and TFN membrane; (b) interfacial polymerization reactions between TMC and MPD, TMC and PIP, respectively.

Since the pioneering work published by Hoek and coworkers in 2007 [28], research interests in TFN membranes have been ever-increasing (Figure 2). Previously, both porous/nonporous inorganic and organic nanomaterials have been employed to construct TFN membranes due to their unique morphologies, structures, surface chemistry and ability to influence cross-linking degree during IP. On the one hand, the incorporation of nanomaterials is able to provide internal nanochannels (e.g., intrinsic inner pores of porous nanomaterials) [28-31] and external nanochannels (e.g., interfacial space between embedded nanomaterials and PA matrix) [32-34], which contribute to the facilitated solvent transport through preferential flow paths. On the other hand, the incorporation of nanomaterials has noticeable impacts on membrane hydrophilicity, roughness, zeta potential and cross-linking degree, which in turn play significant roles in membrane permeability, selectivity and antifouling performance [35]. The potential of fabricating advanced TFN membranes with numerous inorganic nanomaterials like carbon-based nanomaterials (e.g., carbon quantum dots [36, 37], graphene oxide [38], carbon nanotubes [39]), metal-based nanomaterials (e.g., Ag [33], TiO_2 [40], ZnO [41], Al_2O_3 [42], MoS_2 [43]) and silicon-based nanomaterials (e.g., zeolites [44], SiO_2 [29], halloysite nanotubes [45]) has been widely investigated. In comparison, organic nanomaterials-based TFN membranes remain less explored. Taking advantages of the greater compatibility with polymer matrix, structural versatility and functionality, more and more attempts have been made to embed organic nanomaterials, such as cellulose nanocrystals, solid/porous polymeric nanospheres, covalent organic frameworks and so forth, in PA layer with elevated performance in recent years [46-51].

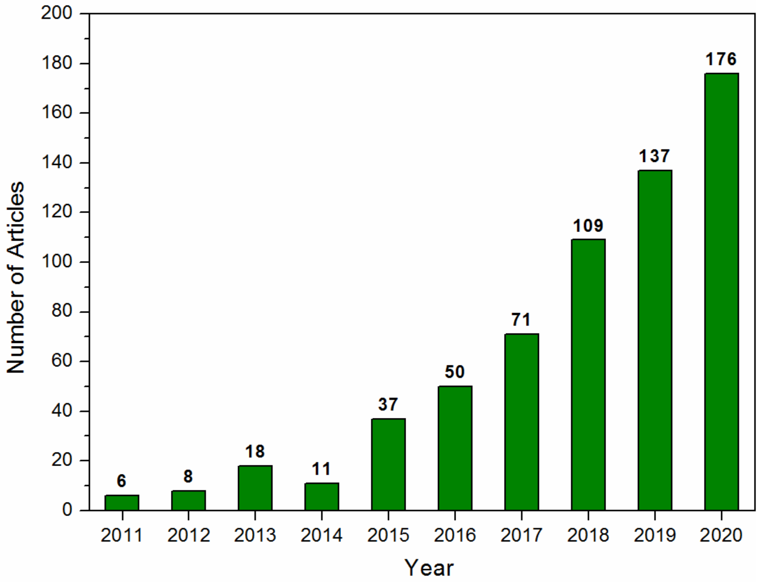

Fig. 2. Number of research documents published in refereed journals on TFN membranes between

2011 and 2020. Source: Web of Science.

Until now, there have been several enlightening reviews related to TFN membranes mainly incorporated with inorganic nanomaterials for desalination and water treatment [18-20, 35, 52-54]. However, no comprehensive review is available so far to focus specifically on organic nanomaterials based TFN membranes. Accordingly, this review will give a survey on recent publications that investigated the performance enhancement of TFN membranes embedded with organic nanomaterials for both aqueous-based media and organic-based media as summarized in Figure 3. We start with the pioneering works of TFN membranes for NF, RO, FO, OSN and OSFO applications and the relevant theoretical supports. This is followed by a detailed discussion on the influence of a variety of solid and porous organic nanomaterials on the properties and performance of the resultant TFN membranes. Of note, the advanced inorganic-organic hybrid nanomaterials, metal organic frameworks (MOFs), are also included due to their significant role in TFN membranes. The synthesis, modification and utilization of functional organic-based nanofillers for constructing state-of-the-art TFN membranes as well as the proposed transport mechanism will be highlighted. At last, current challenges and future prospects for further advancement in this field are outlined.

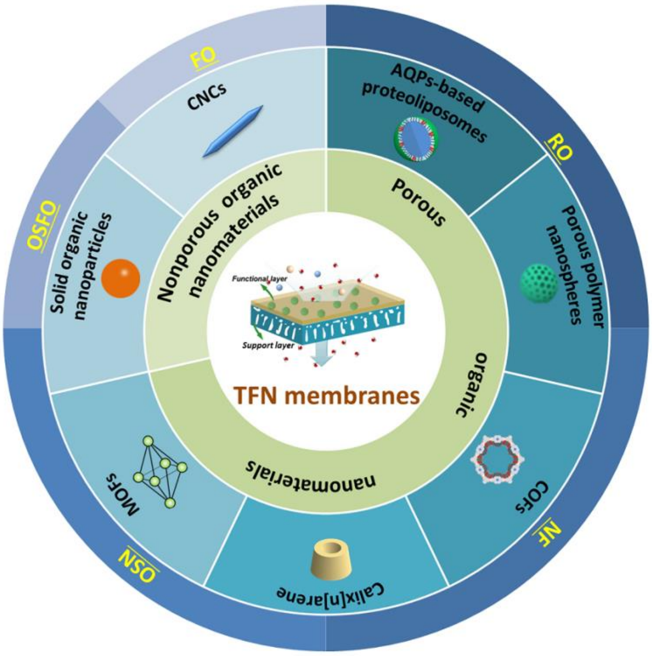

Fig. 3. Summary of TFN membranes with organic-based nanomaterials for aqueous and organic

solvent filtration.

2. Pioneering TFN membranes for different applications

2.1. TFN membranes in NF/RO/FO processes for aqueous-based media

TFC membrane with PA selective layer formed by IP is the core of RO and NF techniques applied to seawater/brackish water desalination and wastewater reclamation [16, 55-57]. Interfacial polymerization of TFN membrane for RO application was first developed by Hoek and coworkers in 2007 [28]. In this pioneering work, super-hydrophilic and negatively charged NaA zeolite nanoparticles with three-dimensional molecular sieve pore network were incorporated into PA layer, which provided preferential water pathways while maintaining high salt rejection. NaA embedded TFN membrane had higher water permeability (2.8×10^{-12} mPa^{-1} s^{-1}) compared to the control TFC membrane (2.1×10^{-12} mPa^{-1} s^{-1}) and TFN membrane with pore-filled zeolite nanoparticles (2.5×10^{-12} mPa^{-1} s^{-1}) without compromising NaCl rejection under the same conditions. The results demonstrated that the molecular sieve pores in NaA play a positive role in water permeation and solute rejection. As the separation mechanism of RO membrane is based on size exclusion and Donnan effect [58], the negative charges of nanoparticles also accounted for the highly maintained salt rejection. It is worth mentioning that Donnan effect plays a more significant role in NF process rejecting charged molecules and multivalent salts than in RO process rejecting monovalent salts. This work provided new insights in designing next generation high-performance RO membrane and useful guidelines for dealing with permeability-selectivity trade-off of TFC membrane.

One of the earliest discussions of TFN NF membrane was reported by Lee et al. in 2008 [59]. Although the authors did not name the obtained membrane as TFN membrane, but the concept for PA-TiO_2 composite membrane was the same as that for the TFN RO membrane proposed by Hoek and coworkers [28]. In the study, TiO_2 nanoparticles were added in organic phase prior to IP which was helpful to confine TiO_2 in PA matrix. The PA-TiO_2 composite membrane possessed higher permeability than the neat membrane due to its improved hydrophilicity. Since those earliest reports were published, marvelous achievements on TFN membranes have been made.

Unlike pressure-driven membrane processes such as RO and NF, forward osmosis (FO) employs osmotic pressure to transport water from a low-concentration feed solution to a high-concentration draw solution [60]. The water-loaded draw solution can be regenerated by RO process or thermal treatment. FO offers advantages of processing feeds with higher salinity, lower fouling tendency and higher flux recovery over pressure-driven membrane processes in brackish/seawater desalination [61]. Thus, it can be potentially applied to treat high-salinity/high-fouling-tendency feed waters (e.g., produced water [62-64]) and for the pretreatment of RO in desalination via a hybrid FO-RO process [65]. The use of TFN membrane for FO aimed at water purification was first reported by Tang and his coworkers in 2012 [66]. Inspired by the superior performance of zeolite-based TFN RO membranes [28, 67], the authors fabricated TFN FO membranes with the incorporation of NaY zeolite nanoparticles in PA rejection layer. With the increase of zeolite loading from 0.02 to 0.1 w/v%, water permeability and FO water flux increased gradually due to the sub-nanometer pores in zeolite nanoparticles as well as the altered IP process and increased membrane surface roughness. However, further increase of zeolite loading caused flux decrease, possibly owing to the formation of a thicker PA layer. Compared to TFC membrane, the TFN membrane was potentially more favorable to be applied for treating feed solutions with higher salinity. This study provided new perspectives and significant guidance to elevate FO membrane performance.

2.2. TFN membranes in OSN/OSFO processes for organic-based media

TFN membranes can not only be applied in aqueous media but also used for organic solvent filtration. Organic solvent nanofiltration (OSN) is an alternative and promising technology for organic solvent recovery and molecular separation in pharmaceutical and refining applications with benefits of high efficiency and eco-friendliness compared to other techniques such as incineration and distillation [68-70]. It is of note that the substrate of TFN membrane used for organic solvent separation must be robust and solvent stable in a broad range of organic solvents, and the commonly used substrate is covalently cross-linked polyimide (including P84 and matrimid) membrane [71]. The first attempt to fabricate TFN membrane for OSN was made by

Sorribas et al. in 2013 [21]. And it was also the first example of employing metal-organic frameworks (MOFs) as fillers in TFN membrane. In this work, MOFs [ZIF-8, MIL-53(Al), NH_2-MIL-53(Al), and MIL-101(Cr)] with particle size in the range of 50-150 nm were embedded in PA layer via IP. Results showed that solvent permeance increased as the porosity and pore size of the added MOFs increased, indicating that MOF pores provided preferential pathways for the solvents. However, all the MOF-based TFN membranes possessed similar rejections (> 90%) with TFC membrane, demonstrating that the formation of non-selective voids was eliminated owing to the good compatibility between the PA matrix and the organic moieties of MOFs. This work opened new avenues for the combination of MOFs with TFC membrane for liquid separations.

The concept of FO can be applied to organic solvent separations using an emerging process named as organic solvent forward osmosis (OSFO). It was first proposed by Lively and Sholl in 2017 [5], and then demonstrated and developed by Chung’s group targeted at recovering valuable products and organic solvent from pharmaceutical streams [24, 72]. Compared to OSN, OSFO has the potential in lowering fouling propensity and treating highly concentrated feed solutions in a more sustainable manner. Nonetheless, very limited work has been done for the development of OSFO membranes with desired performance so far [24, 64]. TFN OSFO membrane was first attempted recently in 2020 by incorporating Calix[n]arene in PA layer [24].

3. Typical organic-based nanomaterials used for constructing advanced TFN membranes

Up to now, a variety of inorganic nanofillers with different size, morphology and properties have been successfully incorporated into PA matrix to fabricate TFN membranes with promoted performance. However, inorganic nanomaterials are prone to agglomerate during IP process and the compatibility between inorganic nanomaterials and polymeric network is poor, leading to difficulties in membrane fabrication and declined separation performance caused by non-selective defects [73-75]. To address this issue, researchers are devoted to surface modifying inorganic nanoadditives with functional groups or polymeric molecules prior to incorporation [76, 77]. Alternatively, organic-based nanomaterials with intrinsic polymeric characteristics, porous structures and versatile functions are considered as promising candidates for constructing advanced TFN membranes, though they are less frequently reported compared to the widely-used inorganic nanomaterials. As the role of the synthesized/modified inorganic nanomaterials on the property and performance of TFN membranes have been comprehensively summarized in several recent reviews [18-20, 35, 52-54], the current review focuses on the function of organic-based nanofillers.

Table 1 summarizes the representative organic nanomaterials for constructing state-of-the-art TFN membranes with enhanced performance. Typically, the selected nanomaterials can be different in shape, while their size should be smaller than or comparable to the thickness of PA layer (usually in the range of tens to hundreds of nanometers [78-80]) to minimize the formation of defects in the rejection layer. Both solid and porous organic nanomaterials with inner pore size ranging from several angstroms to several nanometers have been used. On the one hand, the nanochannels at the nanofillers/PA matrix interface [34, 47, 81-83] and/or the intrinsic nano/meso-pores of porous nanofillers [30, 49-51, 84] account for the increased membrane permeability by providing preferential flow paths. Notably, the size of the introduced selective nanochannels should be appropriate enough to ensure the efficacy of salt rejection. On the other hand, the incorporated nanomaterials are generally hydrophilic [46, 50, 81-83, 85, 86] and able to increase crosslinking degree [46, 51], reduce thickness [24, 87] and roughness [81, 83] of the resultant PA layer, which also favor membrane permeate flux, rejection and antifouling performance. In some cases, negatively charged nanomaterials are used to enhance (or well-maintain) salt rejection and improve di-/mono-valent salt selectivity by forming a more electronegative surface [46, 50, 81, 82]. To further reinforce the compatibility with PA matrix and membrane stability, organic nanomaterials with intrinsic or introduced functional groups can be robustly embedded in PA matrix via covalent bonds [48, 49].

Table 1

Representative organic nanomaterials for the fabrication of advanced TFN membranes via IP technique.

Organic-based nanomaterials	Nanomaterial properties	Aqueous-organic monomers	Chemical interactions with PA matrix	Application	Membrane performance summary	Ref
CNCs[a]	Rod-like structure length: 190 ± 90 nm diameter: 15 ± 5 nm hydrophilic	MPD-TMC*	-	RO	Doubled water flux without significantly compromising salt rejection Better antifouling performance	[86]
CNCs	Rod-like structure length: 200-300 nm width: 15-30 nm hydrophilic negatively charged	PIP*-TMC	Covalent bond	NF	Enhanced permeability, salt rejection and antifouling properties	[46]
TOCNs[b]	Length: 101 ± 8 nm diameter: 7 ± 1 nm	MPD*-TMC	-	RO	Increased water flux and salt rejection	[34]
ZPNPs[c]	Spherical size: 350 nm abundant hydroxyl, carboxyl, and sulfobetaine groups	PIP*-TMC	Covalent bond	NF	Higher water permeability Enhanced NaCl/Na_2SO_4 selectivity Improved antifouling performance	[81]
ZNGs[d]	Spherical size: 100-200 nm surper-hydrophilic	PIP*-TMC	Covalent bond Ionic bond	NF	Increased water permeability High di-/mono-valent salt and antibiotic molecule selectivity Exceptional stability and antifouling property	[82]
ADNPs[e]	Quasi-spherical shape mean diameter: ~90 nm abundant catechol, amine, and sulfobetaine groups	PIP*-TMC	Covalent bond	NF	High water permeance and good selectivity for di-/mono-valent salts Excellent fouling resistance and cleaning recovery property	[83]
PDP[f] NPs	Spherical controllable size and morphology abundant amine and catechol groups	PIP*-TMC	Covalent bond	NF	High water permeability and salt selectivity Enhanced antifouling property	[47]
HZNCs[g]	Core-shell structure AD[l]: 102.6 nm internal nanovoid diameter: 50-80 nm hydrophilic	PIP-TMC*	-	NF	Greatly improved water permeation Slightly increased ionic rejection Good antifouling resistance to proteins	[88]
Polymersomes	Spherical hollow structure AD: ~200 nm average size of hollow structure: ~100 nm	MPD*-TMC	-	RO	Enhanced water flux and better NaCl rejection under both low and high salinity conditions	[51]
NMPS[h]	Amino-functionalized mesoporous nanospheres AD: 66 ± 5 nm mesopore size: 5.6 nm	MPD*-TMC	Covalent bond	RO	Improved water flux High NaCl rejection	[49]
MMP[i]	Interconnected network structure particle size: 20-35 nm pore size: ~13 Å	MPD-TMC*	Covalent bond	RO	Higher water flux and similar salt rejection Good chlorine resistance	[85]
COF (SNW-1)	Sphere-like AD: ~30 nm major pore size: ~5 Å hydrophilic	PIP*-TMC	Covalent bond	NF	Increased pure water flux Promising long-term stability	[89]
COF (SNW-1)	Average size: ~20 nm	MPD*-TMC	Covalent bond	OSN	Enhanced solvent permeance Excellent solvent resistance	[84]
COF-COOH	Sphere-like size: 60-72 nm hydrophilic negatively charged	MPD*-TMC	Covalent bond	FO	Four-fold water flux Synchronously improved reverse flux selectivity	[50]
COF (TpPa2)	Diameter: 40–60 nm thickness: ~5 nm d-spacing: ~0.36 nm	MPD*-TMC	Covalent bond	RO	Triple water permeability Improved H_2O/NaCl selectivity Outstanding chlorine resistance Excellent anti-bacterial	[87]

					efficiency	
STCAss[j] SCA[k]	Hollow cup-like structure water-soluble	MPD*-TMC	Ionic bond	OSFO	High rejection of draw solutes Higher ethanol fluxes and lower reverse solute fluxes	[24]

* indicates that the nanomaterial is added in the aqueous or organic phase;
\- indicates chemical bonding is not reported in the literature;
[a] CNCs-cellulose nanocrystals, [b] TOCNs-2, 2, 6, 6-tetramethylpiperidine-1-oxyl-oxidized cellulose nanocrystals, [c] ZPNPs-zwitterionic polyelectrolyte nanoparticles, [d] ZNGs-zwitterionic nanogels, [e] ADNPs-zwitterionic dopamine nanoparticles, [f] PDP NPs-polydopamine-piperazine nanoparticles, [g] HZNCs-hollow zwitterionic nanocapsules, [h] NMPS-amino-functional mesoporous polymer nanospheres, [i] MMP-metal-induced ordered microporous polymer, [j] STCAss-sulfothiacalix[4]arene, [k] SCA-sulfocalix[4]arene, [l] AD-average diameter.

3.1. Nonporous organic nanomaterials

The properties (e.g., hydrophilicity, electronegativity) of nonporous organic nanomaterials and their interactions with PA matrix to a large degree determine the separation performance of nonporous organic nanomaterials-based TFN membrane. In this section, typical solid organic nanomaterials, including biocompatible cellulose nanocrystals, hydrophilic zwitterionic nanoparticles and facilely-synthesized mussel-inspired nanoparticles, are integrated in PA layers to construct advanced TFN membranes. The impacts of these nanomaterials on the microstructures, properties and performance of the resultant TFN membranes are highlighted and discussed.

3.1.1. Cellulose nanocrystals (CNCs)

Cellulose nanocrystals (CNCs) are natural rod-like particles derived from acid hydrolysis of different sources, such as wood, cotton, hemp, wheat, and straw [90]. The chemical structure of cellulose and scanning electron microscope (SEM) image of CNCs are shown in Figure 4a and Figure 4b, respectively. They are considered as low-cost, renewable and biodegradable materials with no/low environmental and health impacts [91]. In addition, CNCs exhibit high aspect ratios, attractive mechanical properties along with high negative zeta potential, highly hydrophilic surface and promising potential for surface modification owing to the presence of hydroxyl groups [46, 92]. These merits make CNCs promising modifiers for improving membrane efficiency for water treatment [46, 86, 93-97].

Asempour et al. fabricated novel CNCs-based TFN membranes by in-situ IP of MPD and TMC containing certain amounts of CNCs [86]. From the brackish water RO experimental results (Figure 4c,d), the best performed membrane with CNCs loading of 0.1 w/v% achieved doubled water flux without dramatically compromising salt rejection (97.8%). The enhanced water flux might result from the improved membrane hydrophilicity and the enlarged effective surface area for permeation. At the highest CNCs content of 0.2 w/v%, the reduced water flux was mainly attributed to the severe blockage of water paths by impermeable CNCs. Besides, the significant decrease in salt rejection at excessive loading was attributed to the defects in PA layer formed by CNCs agglomerates. Almost at the same time, CNCs-based TFN NF membranes were developed [46]. Due to the enhanced hydrophilicity, electronegativity, cross-linking degree and the reduced pore size, the permeability and monovalent salt rejection increased while divalent salt rejection kept unchanged with increased CNC content. In addition, both the CNCs-based TFN RO and NF membranes showed an improved fouling resistance. Nonetheless, further study is required to have a better understanding of the interactions between CNCs with PA matrix as well as the impact of the optimized loading content on membrane separation performance and long-term stability.

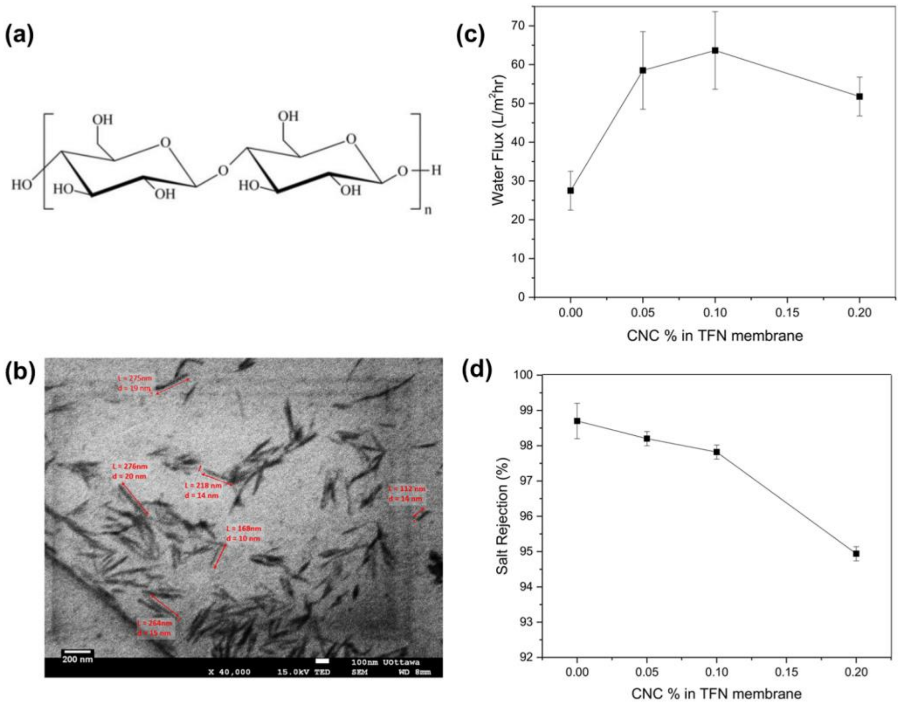

Fig. 4. (a) Molecular structure of cellulose (The figure is reprinted from Ref. [98] with copyright permission); (b) Transmission Electron Detector SEM image of CNC particles (The figure is reprinted from Ref. [86] with copyright permission); (c) water flux and (d) salt rejection of the TFC membrane and CNC-TFN membranes with different CNC loadings. Each point represents the average flux/rejection of at least 3 tested membrane samples, each with 17.52 cm^2 active area (The figure is reprinted from Ref. [86] with copyright permission).

Liu et al. employed carboxylated cellulose nanocrystals (C-CNCs), which have better dispersibility, hydrophilicity and electronegativity than CNCs due to the -COOH groups on their surface, to investigate the role of nanomaterial location in the active layer versus in the support layer of the TFC NF membranes [99]. Results show that higher permeate flux was achieved by incorporating C-CNCs in the active layer of the TFC membranes, while blending C-CNCs in the support layer improved membrane salt rejection and mechanical strength. This work provides new insights for targeted designing and constructing TFC membranes assisted by environmental benign nanomaterials for water treatment.

Controlling nanomaterial/polymer interfacial nanovoids is an effective strategy in tuning molecule transport and selectivity of TFN membrane. Recently, 2, 2, 6, 6-tetramethylpiperidine-1-oxyl-oxidized cellulose nanocrystals (TOCNs) were applied to form TFN RO membranes during IP via a monomer dispersion method [34]. Results showed that the increase in water flux was attributed to the formed nanochannels at nanocrystal/polymer interface that allowed rapid water transport, while the salt rejection was determined by the size of nanochannels which depended on the strength of the nanocrystal/polymer interactions. The presence of carboxyl groups on TOCNs surface was responsible for the high salt rejection due to the enhanced hydrogen bonding between TOCNs and PA matrix. The best-performing TFN membrane at TOCNs loading of 0.5 wt% had a water flux increased by 260% and a higher salt rejection (98.98%) compared to the control TFC membrane. Moreover, further optimization of water flux and salt rejection can be achieved by including other surface functionalized-CNCs in PA matrix [34].

3.1.2. Other solid organic nanofillers

Solid organic nanoparticles are propitious to be used in TFN membrane manufacture due to their good compatibility with PA matrix and versatile structures and functionalities. For instance, An and co-workers used zwitterionic polyelectrolyte nanoparticles (ZPNPs), which were synthesized by ionic crosslinking, as building blocks to fabricate TFN membranes with interfacial water channel structures between ZPNPs and PA matrix [81]. The ionic crosslinking degree and zwitterionic groups' content of ZPNPs can be dedicatedly controlled to further improve membrane water permeability and di/monovalent salt selectivity by increasing the external nanochannels. Antifouling performance of ZPNPs-based TFN membrane was found to be better than that of the control TFC membrane due to its increased surface hydrophilicity, electronegativity and reduced surface roughness.

Similarly, the same group of researchers facilely synthesized soft polymeric particles, zwitterionic nanogels (ZNGs), via surfactant-free emulsion polymerization and embedded them into PA matrix to fabricated TFN NF membranes with simultaneously improved permeability and selectivity coupled with excellent stability and anti-fouling properties [82]. In this work, the mechanism of improvement in separation performance with the assistance of ZNGs was studied in depth by the positron annihilation spectroscopy. The microstructures with both nano-cavities and free-volume pores were identified in the PA layer (Figure 5d). As shown in Figure 5b, the free-volume size, which was corresponding to the molecular scale space between PA chains, was maintained at 2.7 ± 0.1 Å. However, the size of the nano-cavities, originated from the interfacial space between ZNGs and polyamide macromolecule aggregates as well as the large chain-to-chain space between polyamide aggregates [100], depended on ZNGs loading similar to water permeability coefficient (Figure 5a). The water flux of ZNGs-based TFN membranes (ZNGTFNMs) increased with the larger nano-cavity size, and the salt rejection increased with smaller free-volume. As a result, the fabricated membrane at ZNGs loading of 0.035 w/v% outperformed TFC membranes reported in literatures (Figure 5c).

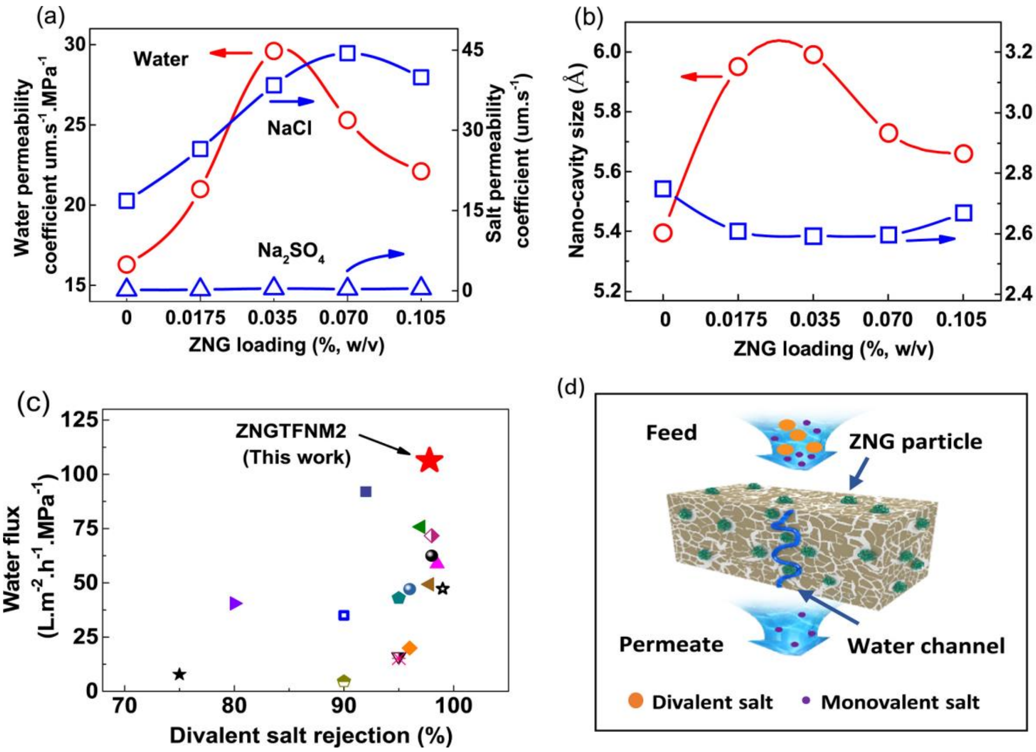

Fig. 5. (a) Water permeability coefficient, and Na_2SO_4/NaCl permeability coefficient of ZNGTFNMs with different ZNG loadings, (b) free-volume and nano-cavity size of ZNGTFNMs with different ZNG loadings, (c) comparison of ZNGTFNM2 with various polyamide membranes reported in previous study, and (d) schematic illustration of the microstructure and permeation performance of ZNGTFNMs. The figure is reprinted from Ref. [82] with copyright permission.

Owing to the unique self-polymerization and adhesion properties of mussel proteins, the potential of mussel-inspired nanoparticles as advanced nanofillers to fabricate TFN membranes has been demonstrated recently. Basically, dopamine can be oxidized into dopaquinone and reacted with amino and thiol groups through Schiff-base and/or Michael addition reaction in alkaline solution to form functional coatings [101-104] or assembled into nanoparticles through covalent and non-covalent interactions [105-107]. A convenient and universal strategy was exploited for synthesizing zwitterionic dopamine nanoparticles (ADNPs) with monomers N-aminoethyl piperazine propane sulfonate (AEPPS) and dopamine. The ADNPs as “building blocks” participated in IP of PIP and TMC on porous substrate to fabricate TFN NF membranes with good perm-selectivity, long-term stability and fouling resistance [83]. Another facile and versatile strategy was proposed to fabricate TFN NF membranes with polydopamine-piperazine (PDP) nanoparticles (NPs) integrated in PA layer, which were formed in-situ by polymerization reaction of dopamine and PIP (Figure 6) [47]. The abundant amines and catechol groups on PDP NPs reinforced their compatibility with PA matrix via covalently reacting with TMC to form amide and ester bonds. The PDP NPs incorporated TFN membrane exhibited competitive NF performance in terms of both high water permeability and salt selectivity, along with enhanced antifouling property against bovine serum albumin. Therefore, facile and universal fabrication of organic nanoparticles based on bio-inspired assembly should be encouraged in further studies for developing promising TFN membranes with conveniently implemented fabrication process and low cost.

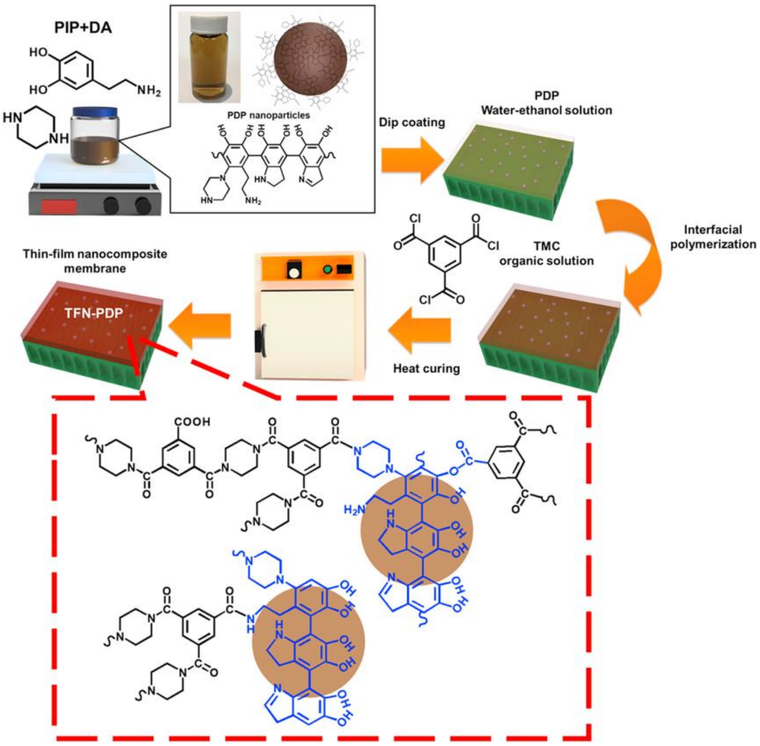

Fig. 6. Schematic illustration of fabricating thin-film nanocomposite membranes with in situ PDP nanoparticles. The figure is reprinted from Ref. [47] with copyright permission.

3.2. Porous organic nanomaterials

In contrast to the impermeable solid organic nanomaterials, the most significant characteristic of porous organic nanomaterials is that they possess well-organized inner pore structures with molecular sieving properties that imparting preferential flow paths for solvent molecules while rejecting solutes. Therefore, the resultant TFN membranes might have greater potential to outperform conventional TFC membranes. In this section, focus is placed on recent advances in TFN membranes embedded with porous organic-based nanofillers, consisting of aquaporin-based proteoliposomes, porous polymer nanospheres, calix[n]arene, covalent organic frameworks and metal organic frameworks. Comments are also provided on further development of TFN membranes incorporated with each category nanomaterials.

3.2.1. AQPs-based proteoliposomes

Aquaporins (AQPs), a family of natural water channel proteins with high water permeability (each water channel can pass ~10^9 water molecules per second) and superior selectivity (the water channel only allows water transport while rejecting solutes) [108-110], are rather attractive for desalination. Since Kumar et al. tossed the concept of fabricating AQP-based biomimetic membranes for the first time [108], tremendous research interest has been generated on AQP-based membranes. Compared to the composite membranes where AQPs assembled in lipid or polymeric bilayer on a porous substrate to form a selective layer, AQP-based TFN membranes are easier to scale up [7]. Similar to the aforementioned TFN membranes, AQP-based TFN RO/FO membranes were fabricated by immersing a membrane substrate in aqueous solution of MPD containing AQP-based proteoliposomes, and then exposing to organic solution of TMC to form a cross-linked PA layer [30]. The resultant membrane with surface area over 200 cm^2 achieved a permeability of ~4 $Lm^{-2}h^{-1}$/bar and a NaCl rejection of ~97%, which were superior to the performance of commercial RO membranes (BW30 and SW30HR). Li et al. extended this approach to hollow fiber membrane with AQP-incorporated proteoliposomes embedded in PA layer in the lumen [111]. The obtained membranes exhibited excellent performance with significantly improved water flux and higher salt rejection in low-pressure RO and FO tests.

One potential concern of AQP-based TFN membranes is the potential denature of AQP proteins, which could adversely impact the long-term membrane stability. A recent 100-day pilot scale test using a real RO feed water showed satisfactory long-term performance even though some flux decline occurred due to fouling [110]. These TFN membranes were able to withstand common cleaning chemical agents, such as ethylenediamine tetraacetic acid, sodium hydroxide and citric acid, but could be sensitive to changes in pressure and temperature. In a separate study [112], the chemically-cleaned AQP-based TFN RO membrane was able to maintain high salt rejection (> 98%), but its water flux dramatically increased possibly caused by the changes in membrane structure and the increased hydrophilicity near the aquaporin. Future studies need to validate the performance stability of AQP-based membranes in a wider range of operation conditions. Besides, methodologies to yield and extract AQPs in high quantities as well as the techniques to produce large-scale robust and defect-free membranes should be further optimized to lower the overall material and manufacture costs.

3.2.2. Porous polymer nanospheres

Owing to the excellent compatibility with polymer matrix as well as the water permeable and selective inner nanochannels, the potential of porous polymer nanospheres in constructing TFN membranes via facile IP technique has been demonstrated. Sun et al. first embedded hollow zwitterionic nanocapsules (HZNCs) into PA layer to fabricate TFN membranes for NF performance improvement [88]. The nanovoid cores of HZNCs resulted in increased membrane internal free volume, which provided numerous short-cut channels for water permeation. Combining with the enhanced membrane external surface area and hydrophilicity, water permeation of the TFN membrane with 19.0 wt% HZNCs increased by 70% and 40% relative to that of the TFC control membrane and the TFN membrane with nonhollow zwitterionic nanoparticles, respectively. In addition, the prepared TFN NF membrane exhibited improved fouling resistance and well-maintained ionic rejection (95% rejection of Na_2SO_4). Interestingly, the authors found that HZNCs was only effective to be added in the oil phase rather than the aqueous phase during IP process. Similarly, Zhu et al. fabricated highly permeable TFN NF membranes by incorporating in-situ formed polydopamine/poly(ethylene glycol) (PDA/PEG) nanocapsules in PA layer [48]. First, PDA was coated on zeolitic imidazolate framework-8 (ZIF-8) nanoparticles via oxidation and self-polymerization of dopamine in alkaline condition. Then, PEG-NH_2 was grafted on PDA coated ZIF-8 by Michael addition and/or Schiff-base reaction, which improved the monodispersity of the particle. As shown in Figure 7, PDA/PEG nanocapsules were formed in PA selective layer as a result of the etching and removal of ZIF-8 cores by the generated acid during IP. This work provides a novel strategy of constructing water preferential channels in selective layer for high performance NF applications. In addition, polymersomes with spherical hollow structure formed by self-assembly of amphiphilic tri-block copolymer were immobilized into PA network of RO membrane [51]. Results showed that the improved void fraction in the selective layer resulting from the highly permeable polymersomes was responsible for the better water permeation, while the tighter PA matrix and the impermeability to NaCl of the polymersome bilayer contributed to the elevated salt rejection. Moreover, the polymersome-based TFN RO membrane outperformed the commercial brackish water and seawater RO membranes (BW30 and SW30).

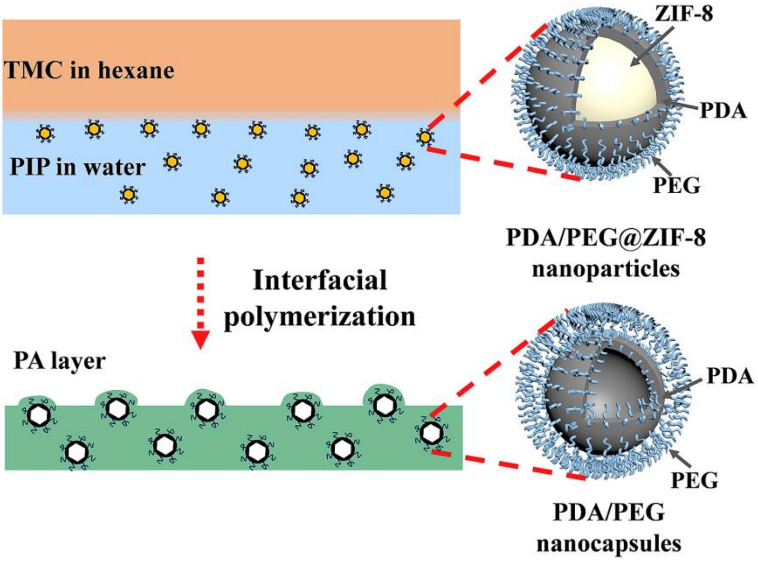

Fig. 7. Schematic diagram for the preparation of TFN membranes with PDA/PEG nanocapsules as fillers. The figure is reprinted from Ref. [48] with copyright permission.

Besides hollow polymer nanocapsules, meso/microporous polymer nanospheres were also synthesized and utilized to construct TFN membranes. In a recent work by Jiang et al., amino-functional mesoporous polymer nanospheres (NMPS) were prepared and incorporated into PA active layer to fabricate TFN RO membranes for high-efficiency desalination [49]. The physicochemical properties of NMPS were characterized first, and the results suggested that the mono-dispersed NMPS with interconnected mesopores of ~5.6 nm provided preferential flow paths for water transport and the abundant amino groups increased the interactions between nanofillers and PA matrix via covalent bonds and hydrogen bonds. Consequently, the TFN membrane with 0.135 mg/mL NMPS in aqueous phase yielded the best performance with a 62% increment of water flux compared to the pristine TFC membrane and a highly maintained NaCl rejection (98.7%), shown in Figure 8a. However, at high loading content, superabundant NMPS caused the formation of connected clusters (Figure 8b), which destroyed the compactness of PA layer or even caused some non-selective defects, leading to the deterioration of salt rejection. Besides, Wang and coworkers incorporated metal-induced ordered microporous polymer (MMP) into PA layer of RO membrane, resulting in improved water flux and chlorine resistance [85]. On the one hand, the micropores of MMP together with the increased hydrophilicity and surface roughness accounted for the elevated membrane water flux. On the other hand, chemical groups such as -Cl and -COOH on the benzene rings of MMP possessed electron-withdrawing and steric hindrance effects, which would protect the amidic N from being attacked by the chlorine [113], thus endowing membrane with improved chlorine resistance especially in alkaline conditions.

From the above, porous polymer nanospheres are promising organic candidates to fabricate TFN water treatment membranes with elevated water flux and high salt rejection. It’s worth mentioning that the membrane performance can be further optimized by precise control and adjustment of the size, porosity and morphology of the aforementioned porous polymer nanospheres. However, long-term running stability of these TFN membranes should be emphasized and characterized for better practical applications.

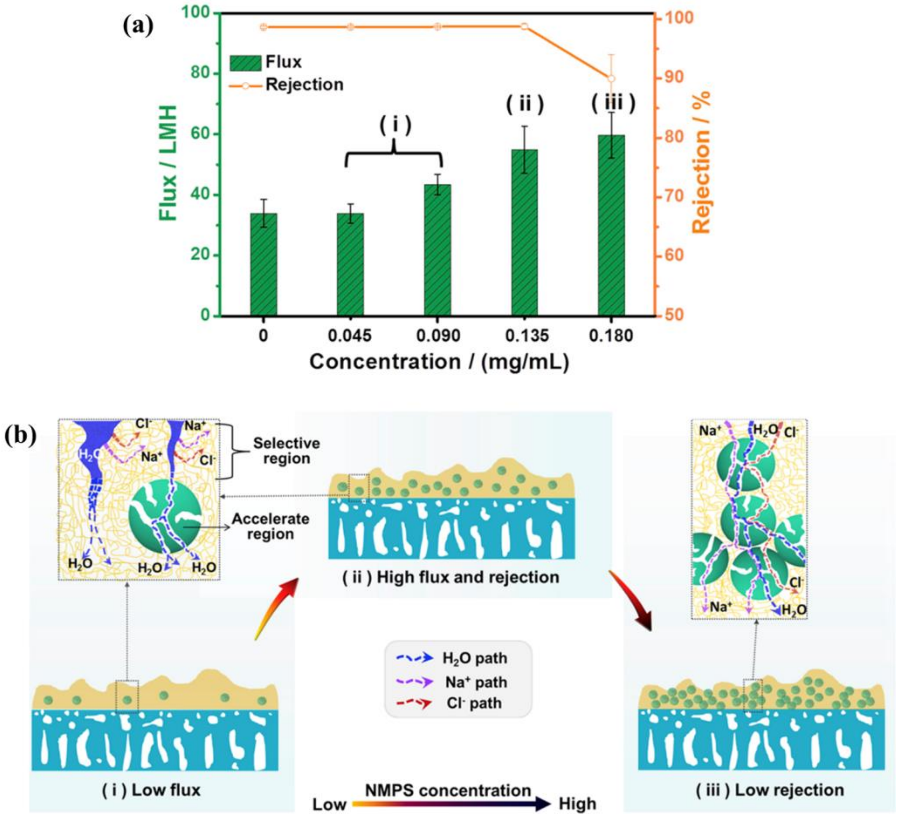

Fig. 8. (a) Performance evaluation for as-prepared TFN membranes in terms of water flux and salt rejection as a function of NMPS loading; (b) The separation mechanism of TFN membranes with different NMPS concentrations. Separation performance was performed using 2 g/L of NaCl as feed solution at 16 bar. The figure is reprinted from Ref. [49] with copyright permission.

3.2.3. COFs

Covalent organic frameworks (COFs), as a new class of crystalline porous materials via strong covalent bonds, have the advantages of high porosity, ordered nanochannels, facilely-tailored functionalities and versatile covalent building combinations, making them promising candidates for constructing new-generation separation membranes [114-116]. Generally, the pore size of reported COFs is in the range of 0.5-4.7 nm, which is suitable for gas separation [117] and removal of divalent salts, dyes and other organic molecules [118]. In the construction of TFN membranes, the pure organic nature of COFs guarantees their excellent affinity with PA matrix, and the pore structures of COFs provide additional pathways for solvent molecules to penetrate, thus enhancing membrane performance in terms of permeability and/or selectivity. In addition, the functional groups of COFs, which determine their hydrophilicity, charge property and interactions with PA matrix, also play a vital role in the obtained membrane performance by altering the properties of PA layer.

Wang et al. reported the first COFs incorporated TFN NF membranes in 2016 [89]. In their work, COFs (SNW-1) with secondary amine groups was integrated into PA layer via filtration-assisted IP of PIP and TMC. Owing to the suitable pore size, high porosity and hydrophilicity of SNW-1, the pure water flux of the obtained COF-based TFN membrane was increased by 92.5%, while the rejection of Na_2SO_4 was maintained above 80%. Besides, SNW-1 covalently linked with PA matrix via the reaction between the -NH- groups and the -COCl groups of TMC, which ensured membrane stability. Li and coworkers employed SNW-1 to fabricate TFN OSN membranes via IP of MPD and TMC followed by chemical crosslinking and solvent activation [84]. The improved hydrophilicity, rougher membrane surface and thinner skin layer of the resultant membrane lead to a 46.7% increment of ethanol permeance and an increased Rhodamine B rejection (up to 99.4%) compared to COF-free membranes. Moreover, thanks to the covalent linkage between SNW-1 and PA network, the TFN membranes exhibited excellent solvent resistance in both long-term static immersion test and consecutive cross-flow filtration test, indicating a promising potential of COF-based membrane in OSN applications.

The potential of COFs in constructing TFN membranes for efficient desalination has also been demonstrated in recent published work. Carboxyl functionalized-COFs (COF-COOH) was synthesized via reaction between TMC and p-phenylenediamine (PPD) and then integrated into PA layer, as shown in Figure 9 [50]. Contributed to the extra water channels, improved hydrophilicity, more negative charge property and smaller mean pore size, the elaborately designed TFN membrane yielded boosted water flux (64.2 $Lm^{-2}h^{-1}$) and simultaneously improved reverse flux selectivity (10.0 L/g), compared to the pristine TFC membrane (15.9 $Lm^{-2}h^{-1}$ and 2.6 L/g, respectively) in FO mode. In the pioneering work by Xu and coworkers, TpPa-2 nanosheets were utilized to construct multifunctional TFN membrane via filtration-assisted incorporation [87]. The resultant membrane exhibited triple water permeability and improved water/solutes selectivity. Besides, it possessed excellent chlorine resistance thanks to the inert methyl groups and the formed chlorine-resistance ternary amide linkage. Moreover, it also exhibited superior anti-microbial performance by surface contact inhibition.

To date, though the studies about COF-based TFN membranes are relatively limited and it remains difficult to fabricate RO membranes with COF integrated into the PA layer, there's still great room to expand COF-based TFN membranes for multiple applications. Besides SNW-1 and TpPa, other chemically stable COFs with pore size around 1 nm (such as TpHz, ACOF-1, COF-300) are also promising in fabricating TFN membranes with enhanced performance, which have not been fully explored yet. Besides, post modifications of the external surface and inner pores of synthesized COFs offer opportunities to rationally tune their physiochemical properties [116]. Moreover, from an industrial point of view, facile and economic synthesis strategies of COFs should be developed, which will benefit the large-scale fabrication of COF-based membranes.

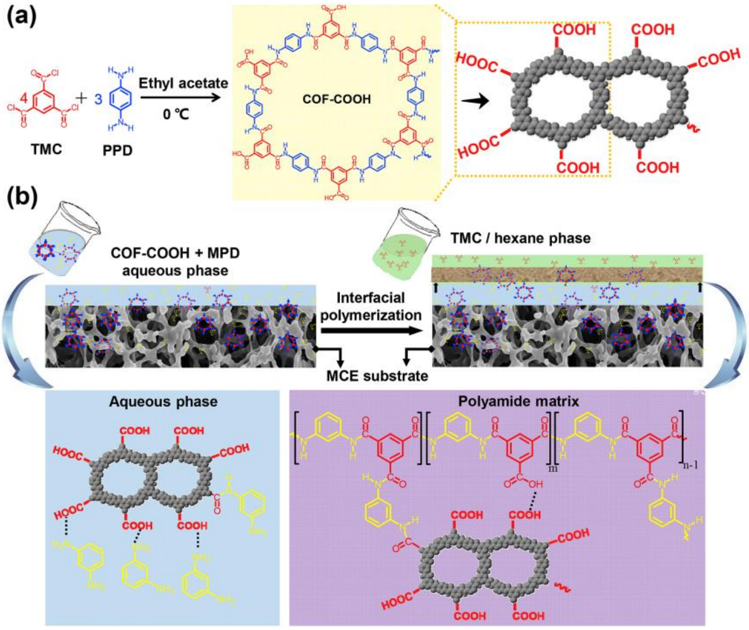

Fig. 9. Schematic illustration of the preparation of (a) COF-COOH and (b) COF-COOH incorporated TFC membrane. The figure is reprinted from Ref. [50] with copyright permission.

3.2.4. Calix[n]arene

Calix[n]arene is a kind of close-loop size-selective macrocyclic molecules, which contains several repeating units of phenolic blocks with a hollow cup-like structure. Taking the advantages of their molecular-tunability and molecular-sieving characteristics, Chung's group designed TFN membranes by ionically bonding sulfothiacalix[4]arene (STCAss) and sulfocalix[4]arene (SCA) in the PA network and explored their application in OSFO [24]. The structures of STCAss and SCA and their interactions with PA network are shown in Figure 10a,b and 10c, respectively. Results showed that the involvement of STCAss and SCA in PA network increased the free volume and reduced the thickness of the selective layer. Combining with their molecular-sieving lower cavities, both STCAss and SCA ensured high rejection of draw solutes. And the STCAss-functionalized TFN membrane possessed an ethanol flux doubling the pristine membrane.

The applications of calix[n]arene had been constrained to areas such as molecular recognition [119], sensor [120], and gas separation membranes [121]. However, the employment of calix[n]arene in TFN membrane for OSFO process sheds light on the potentials of calix[n]arene in molecularly designing pressure-driven TFN membranes with simultaneously improved permeability and selectivity for desalination, wastewater treatment and solvent reclamation.

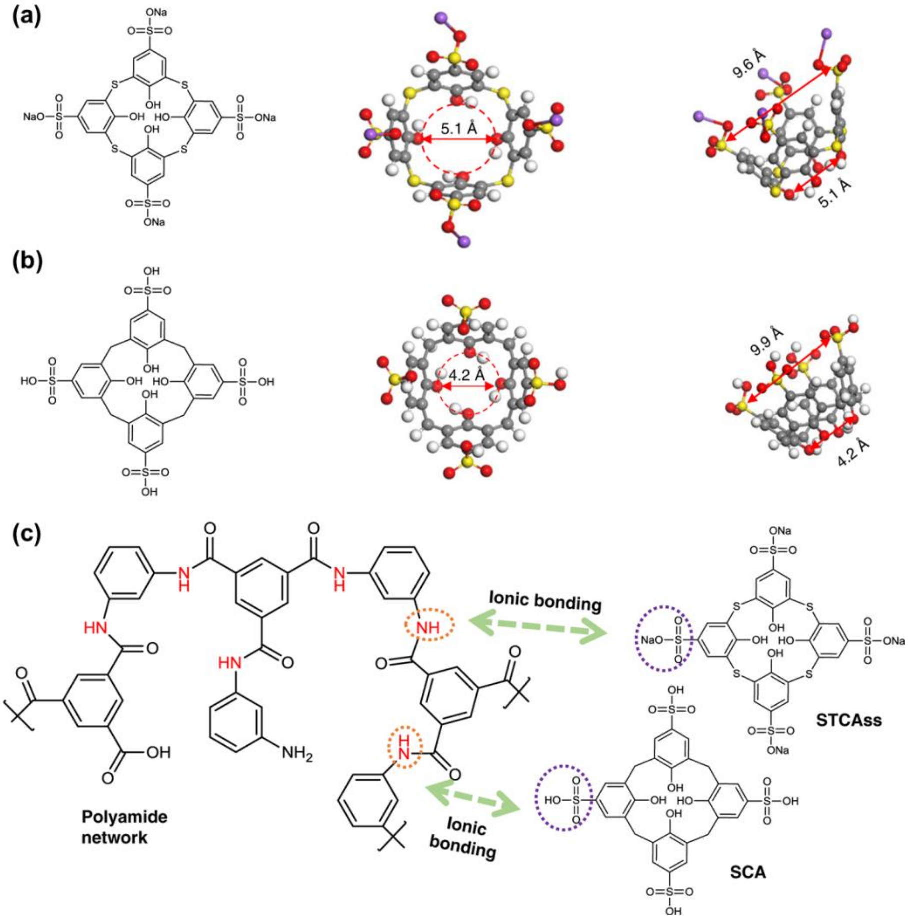

Fig. 10. Molecular structures of (a) STCAss and (b) SCA; (c) illustrations on the interactions between polyamide network and STCAss/SCA. The figure is reprinted from Ref. [24] with

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3.2.5. MOFs

Metal organic frameworks (MOFs) are hybrid organic-inorganic solid compounds, constructed by metal ions/clusters and organic linkers [122]. Considering the inspiring merits of the high surface area, controlled porosity, tunable chemical composition, flexible structure and good affinity for organic polymers [21, 123], MOFs are expected to be ideal porous nanofillers for fabricating TFN membranes used in organic separation as well as diversified water purification field as tableted in Table 2.

Sorribas et al. first incorporated MOFs [ZIF-8, MIL-53 (Al), NH_2-MIL-53 (Al) and MIL-101(Cr)] in PA layer for OSN application with enhanced permeance and maintained rejection [21]. Since then, the number of studies on MOFs-based TFN membranes has been rapidly expanding. New MOFs [MIL-101(Cr), MIL-68(Al) and ZIF-11] were found by Echaide-Gorriz et al. for fabricating TFN OSN membranes [124]. The authors pointed out that in addition to the porous structure of MOF, membrane hydrophilicity as well as the solvent-membrane and solute-membrane interactions also significantly influenced the OSN permeance. In a subsequent work, Echaide-Górriz et al. simultaneously embedded MIL-101(Cr) and ZIF-11 in one PA layer to construct TFN OSN membrane with versatile performance [125]. Zr-MOFs with excellent chemical and thermal stabilities, like UiO-66-NH_2 and UiO-66, are also ideal fillers for improving molecular separations during OSN [126]. To further improve the dispersibility of MOFs in nonpolar solvents and interfacial compatibility between MOFs and polymer matrix, UiO-66-NH_2 was surface-modified with dodecyl aldehyde (DA) and then used to construct TFN OSN membrane with defect-free ultrathin layer [127]. As a result, the dimethyl formamide-activated TFN membrane prepared with 0.15 wt% surface modified UiO-66-NH_2 (DA-UiO-66-NH_2) in organic phase possessed superior OSN performance with methanol permeance of 20 $Lm^{-2}h^{-1}$/bar and tetracycline rejection of about 99%, demonstrating its great potential to be applied in pharmaceutical industrial. However, to further validate the function of surface modification of UiO-66-NH_2, the OSN performance of the control TFN membrane incorporated with unmodified

UiO-66-NH_2 should be investigated and compared as well.

MOFs used to construct TFN membrane for water treatment should be hydrostable, such as ZIF-8, MIL-101 (Cr) and UiO-66. Hydrophobic, porous ZIF-8 based TFN membrane for RO application was investigated by Pinnau's group [128]. It was found that hydrophobic microporous nanofillers (e.g., ZIF-8, carbon nanotubes) yielded higher water permeance than the hydrophilic ones (e.g., zeolite) because no friction in the hydrophobic pores influenced water permeation [129-131]. In addition, with the incorporation of ZIF-8 in PA layer, a less cross-linked and more hydrophilic selective layer was formed, which also accounted for the enhanced permeability. Zhu et al. incorporated poly(sodium 4-styrenesulfonate) (PSS) modified ZIF-8 (mZIF) in a PA layer for NF application [132]. The hydrophilic mZIF could evenly disperse in aqueous solution of PIP and the organic moiety of mZIF ensured a good compatibility with PA matrix, which benefited for the formation of a stable selective layer atop the porous support. The incorporation of hydrophilic mZIF furnished PA layer with a retiform morphology and a more hydrophilic and electronegative surface. Consequently, the mZIF-functionalized TFN membrane possessed significantly higher water permeability, and high retentions of Na_2SO_4 and reactive dyes. Xu and coworkers fabricated MIL-101 (Cr) embedded TFN RO membranes with high water permeability and stability [133]. The hydrophilic, porous MOF provided direct water channels and changed PA properties (morphologies, roughness, crosslinking degree and wettability), resulting in increased water flux up to 44%. Besides, the good compatibility between organic linkers of MIL-101 (Cr) and PA matrix benefited for high salt rejection (> 99%) and long-term stability. Thanks to the well-defined sub-nanometer pores as well as excellent chemical and thermal stabilities [134-136], UiO-66 is another popular MOF to be incorporated in PA layer. Ma et al. demonstrated that UiO-66 based TFN membranes exhibited superior permeability, rejection and FO performance [31]. In the research by Li and coworkers [137], tannic acid (TA) was employed to modify UiO-66-NH_2 via Michael addition/Schiff base reaction prior to interfacial polymerization. Owing to the promoted PA matrix-MOFs compatibility along with enhanced membrane hydrophilicity, TFN membranes with proper TA modified UiO-66-NH_2 exhibited simultaneously elevated membrane permeability and selectivity compared to pristine TFC membranes. Since TA could heal the non-selective defects in PA layer, TFN membranes with TA modified UiO-66-NH_2 maintained high rejection at high nanofiller dose, while membranes with the unmodified UiO-66-NH_2 failed to.

In addition to elevate water flux meanwhile maintain high salt rejection, researchers also dedicated to improving boron removal efficiency of RO membranes with the assistance of UiO-66 in PA layer [138]. Boron concentration in drinking water and irrigation should be less than 0.5 mg/L to meet the requirements of human health and plant growth, necessitating further enhancement of boron rejection by RO membrane [139]. UiO-66 could interact with boric acid by chemisorption and has a stronger adsorption capacity than many conventional adsorbents. It was found that the adsorbed boron had a pore narrowing effect on the sub-nanometer pores of UiO-66, which decreased the effective pore size thus increased the boron rejection (Figure 11).

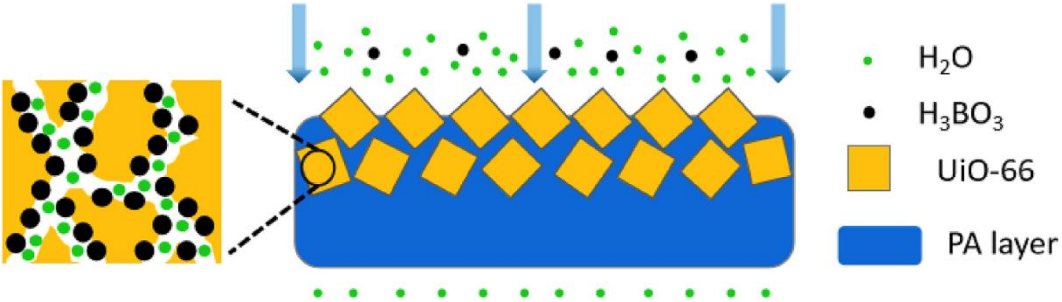

Fig. 11. Boron enhancement mechanism in UiO-66 TFN membrane. The figure is reprinted from Ref. [138] with copyright permission.

Hybrid nanocomposites, which integrate the virtues of individual nanomaterials to deliberately tailor material functions for rational membrane design, are also attractive to be used in enhancing membrane performance. For instance, researchers applied ZIF-8/graphene oxide (GO) in the fabrication of antimicrobial TFN NF membranes [140]. The in situ growth of ZIF-8/GO nanosheets was realized via the coordination between Zn^{2+} of ZIF-8 and carboxyl groups of GO, and then embedded into membranes as multifunctional antimicrobial agent. ZIF-8/GO not only enhanced membrane separation efficiency in terms of improved permeability and well-maintained selectivity, but also prolonged membrane service life due to its effective antimicrobial activity. Results indicated that ZIF-8/GO hybrid nanosheets had a stronger antimicrobial activity than the individuals. As shown in Figure 12a, the antimicrobial activity of GO-based TFN membrane was very limited, owing to its inadequate exposure on membrane surface. However, ZIF-8 and GO could synergistically improve membrane antimicrobial activity by oxidative stress of GO and the release of Zn^{2+} (Figure 12b). This work suggested new pathways for constructing multifunctional TFN membranes with ZIF-8 based nanocomposites.

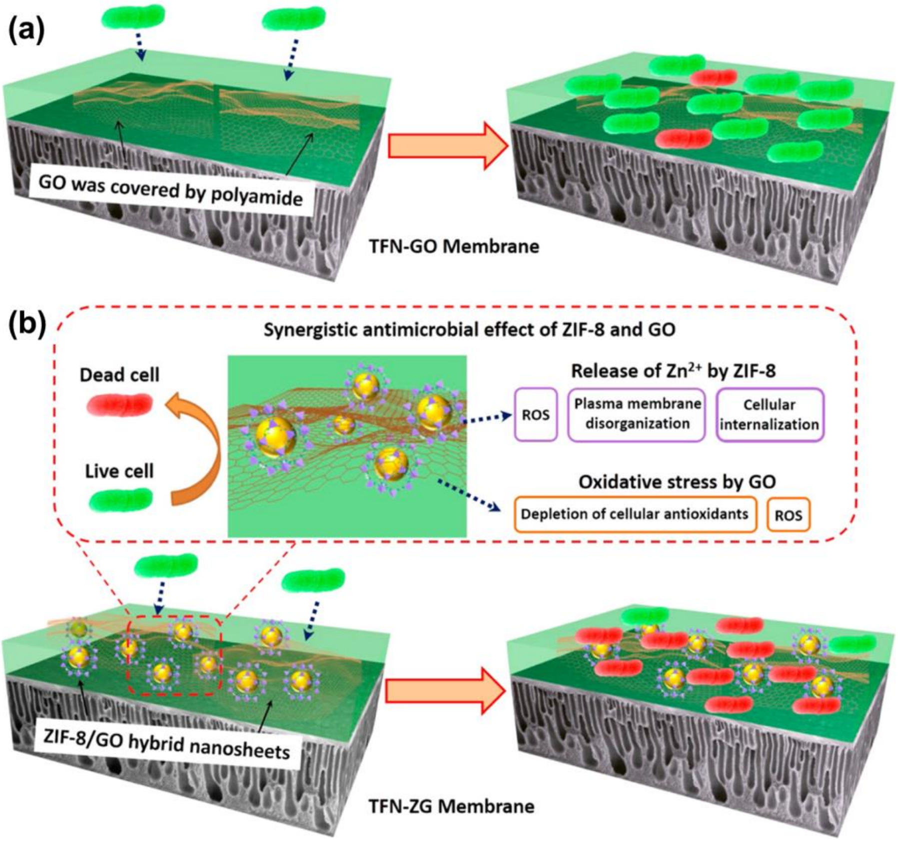

Fig. 12. Schematic diagrams for the antimicrobial mechanism of TFN-GO membranes (a) and TFN-ZIF-8/GO membranes (b). The figure is reprinted from Ref. [140] with copyright permission.

Optimizing the way of loading filler nanomaterials in PA layer is also of vital importance in designing promising TFN membranes, because conventional method via dispersing nanofillers either in aqueous phase or organic phase prior to IP usually lead to the limited loading and heterogeneous localization of functional nanofillers. Aimed to reduce the usage of costly nanomaterials and maximize their superiority, several innovative strategies of positioning MOFs in selective layer have been proposed. Goethem et al. used evaporation-controlled filler positioning (EFP) method to incorporate ZIF-8 into PA layer (Figure 13) and achieved a 220% permeance increase without losing rejection compared to the control TFC membrane [141]. Of note, MOF concentration required for fabricating the optimal TFN membrane reduced 80 times compared to other reported ZIF-8 based TFN membranes. Navarro and coworkers positioned homogeneous and continuous MIL-101(Cr) monolayer between PA layer and cross-linked polyimide support via Langmuir-Schaefer technique to fabricated TFN membrane for OSN with an exceptional increase in methanol permeance and a high dye rejection [142]. The novel method required negligible loading of MOFs, less than 82% of that used by Goethem et al [141]. In addition to EFP and Langmuir-Schaefer methods, other techniques such as layer-by-layer method [143], dip-coating [144], vacuum filtration [145] as shown in Table 2, were also reported as attractive alternatives to the conventional preparation protocol of MOF-based TFN membranes. These innovative methods present new opportunities to dramatically enhance separation performance of TFN membranes meanwhile minimize the fabrication cost and efforts.

The distinct advantages of MOFs (e.g., highly porous structure, molecular sieving property, mild synthesis conditions, tunable chemical functionality and favorable polymer affinity) along with the obtained promising results demonstrate the potential use of MOFs in advanced TFN membranes, which deserves more intensive research efforts in the future. One of the major challenges to further improve MOF-based TFN membrane efficiency is to establish a balance between the loading amount, the dispersibility of MOFs and the separation performance. To address this issue, rational surface modification of MOFs and optimizing the way of MOFs loading are considered to be effective measures. Moreover, functionalized MOFs and MOF-based nanocomposites are promising in achieving multifunctionality and wider applications of the resultant TFN membranes. Besides, more studies on the long-term running performance of MOF-based TFN membranes under practical conditions as well as developing cost-effective design strategies are required to promote their industrial applications.

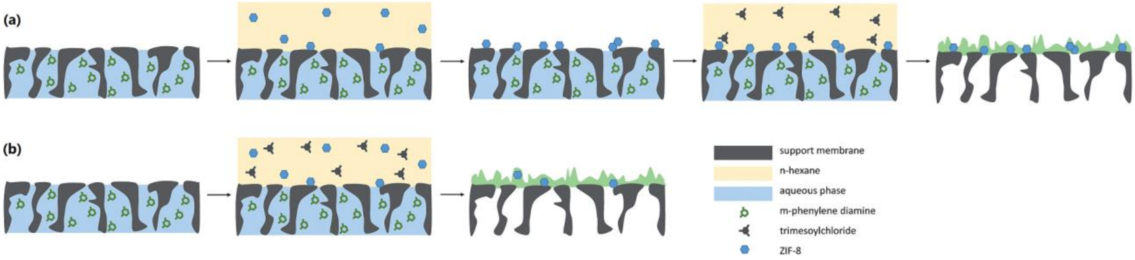

Fig. 13. Schematic representation of (a) the evaporation-controlled filler positioning (EFP) and (b) the conventional TFN membrane preparation protocol. The figure is reprinted from Ref. [141] with copyright permission.

Table 2

Incorporation of MOFs in PA Layers of TFN membranes via conventional IP and innovative techniques to improve membrane efficiency.

MOFs	MOFs properties	MOFs incorporating techniques	Optimal loading content	Application	Membrane performance elevation	Ref
ZIF-8 NH_2-MIL-53 (Al) MIL-53(Al) MIL-101(Cr)	Particle size: 50-150 nm ZIF-8: hydrophopbic others: hydrophilic	Dispersion in the organic phase	-	OSN	Increased solvent permeance without sacrificing rejection	[21]
MIL-101(Cr) MIL-68(Al) ZIF-11	Size: 70, 103 and 79 nm ZIF-11: hydrophopbic others: hydrophilic	Dispersion in the organic phase	-	OSN	Improved methanol permeance	[124]
MIL-101(Cr) and ZIF-11	Size: 173 and 79 nm MIL-101(Cr): hydrophilic, 12–16 Å apertures connected to cages of 29 and 34 Å ZIF-11: hydrophopbic, 14.6 Å pores connected through 3.0 Å apertures	Dispersion in the organic phase	-	OSN	An intermediate performance with improved rejections and permeances	[125]
MIL-101(Cr)	Octahedral particle size: ~200 nm, 1.2 nm pentagonal/1.6 nm hexagonal openings and 2.9 nm/3.4 nm diameter cages Hydrophilic	Dispersion in the organic phase	0.05% (w/v)	RO	Water permeance increased by 44% NaCl rejection remained higher than 99%	[133]
ZIF-8	Rhombic dodecahedron, particle size: ~200 nm 11.6 Å cavity cages, 3.4 Å pore apertures Hydrophobic, hydrothermal stable	Dispersion in the organic phase	0.4% (w/v)	RO	Water permeance increased by 162% NaCl rejection remained high	[128]
mZIF	Sharp hexagonal facets, mean size: 58.8 nm Good dispersibility in water, hydrophilic Negatively charged	Dispersion in the aqueous phase	0.10% (w/v)	NF	Water permeability increased by ~115% Good salt selectivity (13.1) and retention of reactive dyes (>99.0%)	[132]
ZIF-8/GO	-	Dispersion in the aqueous phase	0.1 wt%	NF	Permeability increased by ~53% Well-maintained rejection Higher antimicrobial activity	[140]
UiO-66	Size: ~50 nm, pore diameter: ~6.1 Å, surface area: 1121.6 m^2/g Negatively charged	Dispersion in the organic phase	0.05% (w/v)	RO	Water flux increased by ~50% Rejection increased marginally Boron rejection increased by ~11%	[138]
UiO-66	Octahedral, average particle size: 512 ± 100 nm Hydrophilic	Dispersion in the organic phase	0.1 wt%	FO	Water permeability increased by 52% Salt rejection maintained at ~95% Water flux increase by 40% and 25% under PRO and FO modes Low solute reverse flux Slightly reduced ICP	[31]
DA-UiO-66-NH_2	Particle size: ~20 nm Better dispersibility in n-hexane than unmodified UiO-66-NH_2	Dispersion in the organic phase	0.15% (w/v)	OSN	Methanol permeance increased by 94% High tetracycline rejection of about 99%	[127]
TA-UiO-66-NH_2	Octahedral, mean size: 173.6 nm	Dispersion in the aqueous phase	0.1% (w/v)	NF	Water permeability increased by 93%	[137]

	Hydrophilic				Higher Na_2SO_4 rejection Better anti-fouling property	
ZIF-8	Average diameter: 75 and 150 nm	Evaporation-controlled Filler Positioning (EFP) method	0.005% (w/v)	RO	Permeance increased by 220% without rejection loss More reproducible filtration performances	[141]
MIL-101(Cr)	Size: 60± 20 nm Hydrophilic	Langmuir−Schaefer Technique	3.8 μg cm^{-2}	OSN	Methanol permeance increased by ~35% Dye rejection higher than 90%	[142]
ZIF-8	Rhombic dodecahedral, average particle size: 150 nm Hydrophobic	Layer-by-layer (LBL) Fabrication	-	NF	Membrane permeance increased by ~142% The rejection reached 99.8%	[143]
ZIF-8 ZIF-67	Size: 70 ± 10 nm, 240 ± 40 nm	Dip-coating	-	OSN	Methanol permeance increased by 150% A high sunset yellow rejection	[144]
UiO-66-NH_2	Size: ~200 nm Hydrophilic	Vacuum filtration	20.5 μg cm^{-2}	NF	Water permeance increased by ~112% A favorable Na_2SO_4 rejection of 97.5%	[145]

4. Existing challenges and future prospects

As discussed above, organic nanomaterials as functional nanofillers show great potential in improving TFN membrane efficiency during aqueous or organic solvent filtration. However, challenges coexist with opportunities. The followings are the daunting challenges encountered and the future prospects of organic nanomaterials based TFN membranes, which should be well considered to make them better serve for the separation filed.

4.1. In-depth mechanism study

The main purpose of embedding organic nanomaterials in PA layer is to further increase membrane flux without significantly compromising solute rejection. The potential of different organic nanomaterials in improving membrane separation performance in terms of permeance and rejection is presented in Table S1. It has been commonly accepted that the hypothesized mechanisms for the enhanced permeance of TFN membranes include: (i) low-resistance solvent transport through additional pathways provided by intrinsic pores of porous nanofillers; (ii) interfacial voids between the nanofillers and the PA matrix; (iii) increased membrane affinity to water (hydrophilicity); (iv) changes in membrane microstructure (cross-linking degree and free volume of PA layer) and morphology (roughness and thickness of PA layer) [146]. However, the role of nanofillers in TFN membranes can be more complicated than commonly believed. Apart from the ideal filler effects, indirect effects related to the IP process are also of paramount importance in determining membrane performance. One is the hydration of filler materials, which could generate local heat once contacting with aqueous phase, altering the IP kinetics and solvent miscibility [147]. Another possible effect could be the degradation of acid sensitive nanofillers such as ZIF-8 by the generated HCl during IP [146]. It might be the degradation product possessing catalytic effect that is responsible for performance elevation rather than the material itself. Besides, nanoporous channels in the selective layer can be tuned by self-sacrificed MOFs (e.g., ZIF-67), which are labile in aqueous environment [148]. The presence of nanofillers can also significantly affects sorption and diffusion of amine monomers during the IP reaction [149-151].

Therefore, the exact role of the nanofillers should be clarified to guide the rational design of advanced TFN membranes. In future studies, enhancement mechanisms of membrane permeability by advanced analytic techniques should be encouraged to better understand the formation and structure of TFN membranes, such as nanoscale visualization and chemical characterization via scanning transmission X-ray microscopy (STXM), free volume analysis via pulsed low energy positron beam system (PLEPS), formation of nanochannels via transmission electron microscopy (TEM). In addition, molecular dynamics (MD) simulation is regarded as a powerful tool to investigate transport behavior and even some physicochemical properties of membrane at molecular level [152-154]. It could aid in a better understanding of monomer transport across the water/oil interface and molecule transport across TFN membrane. By combining with experimental results, MD simulation will facilitate the development of advanced membrane technology, which deserves dedicated efforts in the future.

4.2. Further performance optimization

The key challenges for fabricating defect-free and optimized TFN membrane lie in the compatibility issue between nanofillers with PA matrix and the dispersity of functional nanomaterials in the selective layer [48, 155]. Undoubtedly, organic nanomaterials have better affinity with PA matrix than hard inorganic nanoparticles, which is advantageous to eliminate interfacial defects. However, they also tend to agglomerate in monomer phase and localize heterogeneously inside PA layer due to their high surface energy and inter-particle interactions, which would cause defects to TFN membrane as well. As a result, membrane rejection decreases considerably at high nanofiller loading. Furthermore, the findings about membrane flux variation are inconsistent in the literatures. When the loading amount of nanomaterials exceeds its optimum, membrane flux can continuously increase with solvent transporting through the defects or decrease due to the resistance caused by the packed nanomaterials or even level off. Nonetheless, the overall membrane performance deteriorates. In addition to the unsatisfactory dispersibility, only a small fraction of nanomaterials are embedded in the PA layer via conventional preparation protocol of TFN membrane, which limits their potential efficacy on boosting membrane performance and poses a great loss of valuable nanomaterials.

To guarantee the homogenous and sufficient incorporation of nanofillers in PA layer, surface modification of nanomaterials and improved filler incorporation method are two effective ways. Water-soluble polymers like PEG brushes and PSS are modified on the surface of nanomaterials aimed to improve their dispersity in aqueous phase, while long alkyl chains are functionalized on their surface for the purpose of increasing the dispersity in organic phase. The modifier molecules could also increase the compatibility between nanomaterials with polymer matrix and form selective microstructures. On the other hand, new methodologies for sufficient loading of functional nanofillers in PA layer are rather appealing for constructing defect-free high-performance TFN membrane with low consumption of nanofillers, such as bio-inspired layer assisted vacuum filtration, evaporation-controlled nanofiller positioning (EFP), dip-coating, layer-by-layer assembly, etc. By designing new types of functionalized nanofillers and employing efficient nanomaterials positioning strategies, TFN membrane performance is expected to be further optimized in the future. Recently, Tang's group analyzed the permeance-selectivity trade-off of more than 300 published papers and established the upper bound relationship for TFC polyamide membranes, which can serve as a benchmark tool for evaluating further development of desalination membranes [12].

4.3. Scalable fabrication process

The economic benefits of using functional nanomaterials must outweigh the cost of membrane development and production [156]. Notably, the selected organic nanomaterials for TFN membrane construction often involve complicated synthesis routes, such as multistep chemical synthesis and polymerization. The special and delicate synthesis procedures can be difficult, time consuming and cost intensive, which increase membrane manufacture cost to some extent. In addition to the cost issue, green and sustainable strategies to synthesize organic nanomaterials are also worth investigating to meet the demand for the scalable fabrication of TFN membranes. Moreover, the perm-selectivity of TFN membrane is most addressed by researchers, while other important properties such as membrane stability, antifouling propensity, antibacterial property and chlorine resistance remain relatively less explored. Nanomaterials need to be properly selected, tailored and multifunctionalized for targeted compounds removal from the feed solution.

From an industrialized perspective, more facile, economic and sustainable strategies should be developed to synthesize functional organic nanomaterials. It is also necessary to utilize the nanofillers more efficiently to avoid the loss of expensive nanomaterials. As a result, the production process of TFN membrane would be conveniently implemented and cost-effective. Besides, favorable properties of TFN membrane with respect to high perm-selectivity, robust stability, improved antifouling/antimicrobial properties, satisfactory chlorine resistance and boron removal efficiency should be emphasized for their targeted applications, as there is no TFN membrane that is universally applicable for any type of liquid filtration applications.

4.4. Membrane stability

Membrane researchers are devoted to developing membrane material not only scalable but stable. However, some of the incorporated organic nanomaterials are not stable enough and might be degraded under real operation conditions, leading to deterioration in membrane performance. Further research should not ignore to monitor membrane stability in long term, such as solvent resistance in OSN, chlorine resistance in desalination, fouling resistance in almost all filtration applications, antimicrobial activity and pH tolerance in specific applications.

In addition, though organic nanomaterials possess good affinity with PA matrix, it is inevitable for them to leach out from TFN membranes into permeate streams during membrane operation owing to the nano-sizes or lack of covalent bond with PA. The leaching of toxic nanomaterials imposes environmental concerns and violates drinking water safety regulations. In this regard, researchers should find facile ways to strongly anchor nanomaterials in the PA layer by chemical bonding (e.g., chemical reaction between amino-functionalized nanomaterials and TMC) or search for bio-inspired nanoparticles and biocompatible and environmentally-friendly nanomaterials as alternatives.

5. Conclusions

Recently, more and more efforts have been made on the fabrication and development of TFN membranes using organic-based nanomaterials to address challenges such as low permeability, compromised selectivity and fouling propensity faced by traditional TFC membranes as well as to remedy the flaws induced by hard inorganic nanoparticles such as interfacial defects between nanofillers and PA matrix. In this review, the applications of the TFN membranes mainly center on desalination, water reuse and organic solvent purification through membrane processes such as RO, FO, NF, OSN and OSFO. Various solid and porous organic-based nanomaterials are utilized to produce TFN membranes through IP by confining them either in aqueous phase or organic phase. It's worthwhile mentioning that MOFs are rather appealing inorganic-organic hybrid porous nanomaterials that deserve intensive research attentions in TFN membrane fabrication. The incorporation of nanomaterials in PA selective layer is not only able to provide additional nanochannels for facilitated solvent transport and well-maintained solute rejection, but also efficient in altering membrane properties, such as surface roughness, hydrophilicity, zeta potential, cross-linking degree, etc., which also prominently determine membrane performance. Despite of the inspiring progress, we have highlighted future research directions for further advancement of organic nanomaterials based TFN membranes. First, in-depth mechanism study with advanced analytic techniques should be encouraged to clarify the exact role of the embedded functional nanomaterials and thus guide the rational design of TFN membranes for targeted applications. Besides, to minimize the cost and efforts associated with membrane fabrication, more facile, economic and sustainable synthesis/modification routes of organic nanomaterials as well as novel strategies of positioning nanofillers with minute quantity and good dispersibility should be developed. Moreover, efforts should also focus on investigating long-term stability, environmental concerns and commercial potential of the TFN membranes incorporated with organic-based nanomaterials.

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.

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References

[1] P. Marchetti, M.F.J. Solomon, G. Szekely, A.G. Livingston, Molecular Separation with Organic Solvent Nanofiltration: A Critical Review, Chem. Rev. 114 (2014) 10735-10806.

[2] D.S. Sholl, R.P. Lively, Seven chemical separations to change the world, Nature 532 (2016) 435-437.

[3] X. Li, Y. Liu, J. Wang, J. Gascon, J. Li, B. Van der Bruggen, Metal-organic frameworks based membranes for liquid separation, Chem. Soc. Rev. 46 (2017) 7124-7144.

[4] D.L. Gin, R.D. Noble, Designing the Next Generation of Chemical Separation Membranes, Science 332 (2011) 674-676.

[5] R.P. Lively, D.S. Sholl, From water to organics in membrane separations, Nat. Mater. 16 (2017) 276-279.

[6] R.J. Petersen, Composite reverse osmosis and nanofiltration membranes, J. Membr. Sci. 83 (1993) 81-150.

[7] Z. Yang, X.-H. Ma, C.Y. Tang, Recent development of novel membranes for desalination, Desalination 434 (2018) 37-59.

[8] Z. Tan, S.F. Chen, X.S. Peng, L. Zhang, C.J. Gao, Polyamide membranes with nanoscale Turing structures for water purification, Science 360 (2018) 518-521.

[9] M.R. Chowdhury, J. Steffes, B.D. Huey, J.R. McCutcheon, 3D printed polyamide membranes for desalination, Science 361 (2018) 682-685.

[10] C.Y. Tang, Y.-N. Kwon, J.O. Leckie, Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes I. FTIR and XPS characterization of polyamide and coating layer chemistry, Desalination 242 (2009) 149-167.

[11] H.B. Park, J. Kamcev, L.M. Robeson, M. Elimelech, B.D. Freeman, Maximizing the right stuff: The trade-off between membrane permeability and selectivity, Science 356 (2017) eaab0530.

[12] Z. Yang, H. Guo, C.Y. Tang, The upper bound of thin-film composite (TFC) polyamide membranes for desalination, J. Membr. Sci. 590 (2019) 117297.

[13] R. Zhang, J. Tian, S. Gao, B. Van der Bruggen, How to coordinate the trade-off between water permeability and salt rejection in nanofiltration?, J. Mater. Chem. A 8 (2020) 8831-8847.

[14] D. Cohen-Tanugi, R.K. McGovern, S.H. Dave, J.H. Lienhard, J.C. Grossman, Quantifying the potential of ultra-permeable membranes for water desalination, Energy Environ. Sci. 7 (2014) 1134-1141.

[15] G. Liu, W. Jin, N. Xu, Two-Dimensional-Material Membranes: A New Family of High-Performance Separation Membranes, Angew. Chem. Int. Edit. 55 (2016) 13384-13397.

[16] M. Elimelech, W.A. Phillip, The Future of Seawater Desalination: Energy, Technology, and the Environment, Science 333 (2011) 712-717.

[17] Z. Yang, P.-F. Sun, X. Li, B. Gan, L. Wang, X. Song, H.-D. Park, C.Y. Tang, A Critical Review on Thin-Film Nanocomposite Membranes with Interlayered Structure: Mechanisms, Recent Developments, and Environmental Applications, Environ. Sci. Technol. 54 (2020) 15563-15583.

[18] D.L. Zhao, S. Japip, Y. Zhang, M. Weber, C. Maletzko, T.-S. Chung, Emerging thin-film nanocomposite (TFN) membranes for reverse osmosis: A review, Water Res. 173 (2020) 115557.

[19] M. Kumar, M.A. Khan, H.A. Arafat, Recent Developments in the Rational Fabrication of Thin Film Nanocomposite Membranes for Water Purification and Desalination, ACS Omega 5 (2020) 3792-3800.

[20] W.J. Lau, S. Gray, T. Matsuura, D. Emadzadeh, J.P. Chen, A.F. Ismail, A review on polyamide thin film nanocomposite (TFN) membranes: History, applications, challenges and approaches, Water Res. 80 (2015) 306-324.

[21] S. Sorribas, P. Gorgojo, C. Tellez, J. Coronas, A.G. Livingston, High Flux Thin Film Nanocomposite Membranes Based on Metal-Organic Frameworks for Organic Solvent Nanofiltration, J. Am. Chem. Soc. 135 (2013) 15201-15208.

[22] H. Abadikhah, E.N. Kalali, S. Behzadi, S.A. Khan, X. Xu, M.E. Shabestari, S. Agathopoulos, High flux thin film nanocomposite membrane incorporated with functionalized TiO_2@reduced graphene oxide nanohybrids for organic solvent nanofiltration, Chem. Eng. Sci. 204 (2019) 99-109.

[23] M. Peyravi, M. Jahanshahi, A. Rahimpour, A. Javadi, S. Hajavi, Novel thin film nanocomposite membranes incorporated with functionalized TiO_2 nanoparticles for organic solvent nanofiltration, Chem. Eng. J. 241 (2014) 155-166.

[24] B. Li, S. Japip, T.-S. Chung, Molecularly tunable thin-film nanocomposite membranes with enhanced molecular sieving for organic solvent forward osmosis, Nat. Commun. 11 (2020) 1198-1198.

[25] K.C. Wong, P.S. Goh, A.F. Ismail, Thin film nanocomposite: the next generation selective membrane for CO_2 removal, J. Mater. Chem. A 4 (2016) 15726-15748.

[26] O. Choi, Y. Kim, J.-D. Jeon, T.-H. Kim, Preparation of thin film nanocomposite hollow fiber membranes with polydopamine-encapsulated Engelhard titanosilicate-4 for gas separation applications, J. Membr. Sci. 620 (2021) 118946.

[27] M.I. Baig, P.G. Ingole, W.K. Choi, J.-d. Jeon, B. Jang, J.H. Moon, H.K. Lee, Synthesis and characterization of thin film nanocomposite membranes incorporated with surface functionalized Silicon nanoparticles for improved water vapor permeation performance, Chem. Eng. J. 308 (2017) 27-39.

[28] B.-H. Jeong, E.M.V. Hoek, Y. Yan, A. Subramani, X. Huang, G. Hurwitz, A.K. Ghosh, A. Jawor, Interfacial polymerization of thin film nanocomposites: A new concept for reverse osmosis membranes, J. Membr. Sci. 294 (2007) 1-7.

[29] J. Yin, E.-S. Kim, J. Yang, B. Deng, Fabrication of a novel thin-film nanocomposite (TFN) membrane containing MCM-41 silica nanoparticles (NPs) for water purification, J. Membr. Sci. 423 (2012) 238-246.

[30] Y. Zhao, C. Qiu, X. Li, A. Vararattanavech, W. Shen, J. Torres, C. Helix-Nielsen, R. Wang, X. Hu, A.G. Fane, C.Y. Tang, Synthesis of robust and high-performance aquaporin-based biomimetic membranes by interfacial polymerization-membrane preparation and RO performance characterization, J. Membr. Sci. 423 (2012) 422-428.

[31] D. Ma, S.B. Peh, G. Han, S.B. Chen, Thin-Film Nanocomposite (TFN) Membranes Incorporated with Super-Hydrophilic Metal- Organic Framework (MOF) UiO-66: Toward Enhancement of Water Flux and Salt Rejection, ACS Appl. Mater. Interfaces 9 (2017) 7523-7534.

[32] H. Ma, C. Burger, B.S. Hsiao, B. Chu, Highly Permeable Polymer Membranes Containing Directed Channels for Water Purification, ACS Macro Lett. 1 (2012) 723-726.

[33] Z. Yang, H. Guo, Z.-k. Yao, Y. Mei, C.Y. Tang, Hydrophilic Silver Nanoparticles Induce Selective Nanochannels in Thin Film Nanocomposite Polyamide Membranes, Environ. Sci. Technol. 53 (2019) 5301-5308.

[34] E.D. Smith, K.D. Hendren, J.V. Haag, E.J. Foster, S.M. Martin, Functionalized Cellulose Nanocrystal Nanocomposite Membranes with Controlled Interfacial Transport for Improved Reverse Osmosis Performance, Nanomaterials 9 (2019) 125.

[35] D.S. Dlamini, B.B. Mamba, J. Li, The role of nanoparticles in the performance of nano-enabled composite membranes - A critical scientific perspective, Sci. Total Environ. 656 (2019) 723-731.

[36] D.L. Zhao, T.-S. Chung, Applications of carbon quantum dots (CQDs) in membrane technologies: A review, Water Res. 147 (2018) 43-49.

[37] S. Li, C. Li, X. Song, B. Su, B. Mandal, B. Prasad, X. Gao, C. Gao, Graphene Quantum Dots-Doped Thin Film Nanocomposite Polyimide Membranes with Enhanced Solvent Resistance for Solvent-Resistant Nanofiltration, ACS Appl. Mater. Interfaces 11 (2019) 6527-6540.

[38] J. Yin, G. Zhu, B. Deng, Graphene oxide (GO) enhanced polyamide (PA) thin-film nanocomposite (TFN) membrane for water purification, Desalination 379 (2016) 93-101.

[39] S.-M. Xue, Z.-L. Xu, Y.-J. Tang, C.-H. Ji, Polypiperazine-amide Nanofiltration Membrane Modified by Different Functionalized Multiwalled Carbon Nanotubes (MWCNTs), ACS Appl. Mater. Interfaces 8 (2016) 19135-19144.

[40] B. Rajaeian, A. Rahimpour, M.O. Tade, S. Liu, Fabrication and characterization of polyamide thin film nanocomposite (TFN) nanofiltration membrane impregnated with TiO_2 nanoparticles, Desalination 313 (2013) 176-188.

[41] A. Al Mayyahi, Thin-film composite (TFC) membrane modified by hybrid ZnO-graphene nanoparticles (ZnO-Gr NPs) for water desalination, J. Environ. Chem. Eng. 6 (2018) 1109-1117.

[42] T.A. Saleh, V.K. Gupta, Synthesis and characterization of alumina nano-particles polyamide membrane with enhanced flux rejection performance, Sep. Purif. Technol. 89 (2012) 245-251.

[43] S. Yang, K. Zhang, Few-layers MoS_2 nanosheets modified thin film composite nanofiltration membranes with improved separation performance, J. Membr. Sci. 595 (2020) 117526.

[44] M.L. Lind, A.K. Ghosh, A. Jawor, X. Huang, W. Hou, Y. Yang, E.M.V. Hoek, Influence of Zeolite Crystal Size on Zeolite-Polyamide Thin Film Nanocomposite Membranes, Langmuir 25 (2009) 10139-10145.

[45] F. Asempour, S. Akbari, D. Bai, D. Emadzadeh, T. Matsuura, B. Kruczek, Improvement of stability and performance of functionalized halloysite nano tubes-based thin film nanocomposite membranes, J. Membr. Sci. 563 (2018) 470-480.

[46] L. Bai, Y. Liu, N. Bossa, A. Ding, N. Ren, G. Li, H. Liang, M.R. Wiesner, Incorporation of Cellulose Nanocrystals (CNCs) into the Polyamide Layer of Thin-Film Composite (TFC) Nanofiltration Membranes for Enhanced Separation Performance and Antifouling Properties, Environ. Sci. Technol. 52 (2018) 11178-11187.

[47] M.B.M.Y. Ang, Y.-L. Ji, S.-H. Huang, K.-R. Lee, J.-Y. Lai, A facile and versatile strategy for fabricating thin-film nanocomposite membranes with polydopamine-piperazine nanoparticles generated in situ, J. Membr. Sci. 579 (2019) 79-89.

[48] L. Zhang, M. Zhang, J. Lu, A. Tang, L. Zhu, Highly permeable thin-film nanocomposite membranes embedded with PDA/PEG nanocapsules as water transport channels, J. Membr. Sci. 586 (2019) 115-121.

[49] X. Song, Y. Wang, C. Jiao, M. Huang, G.-H. Wang, H. Jiang, Microstructure regulation of polyamide nanocomposite membrane by functional mesoporous polymer for high-efficiency desalination, J. Membr. Sci. 597 (2020) 117783.

[50] L. Xu, T. Yang, M. Li, J. Chang, J. Xu, Thin-film nanocomposite membrane doped with carboxylated covalent organic frameworks for efficient forward osmosis desalination, J. Membr. Sci. 610 (2020) 118111.

[51] S. Qi, W. Fang, W. Siti, W. Widjajanti, X. Hu, R. Wang, Polymersomes-based high-performance

reverse osmosis membrane for desalination, J. Membr. Sci. 555 (2018) 177-184.

[52] M.R. Esfahani, S.A. Aktij, Z. Dabaghian, M.D. Firouzjaei, A. Rahimpour, J. Eke, I.C. Escobar, M. Abolhassani, L.F. Greenlee, A.R. Esfahani, A. Sadmani, N. Koutahzadeh, Nanocomposite membranes for water separation and purification: Fabrication, modification, and applications, Sep. Purif. Technol. 213 (2019) 465-499.

[53] H. Saleem, S.J. Zaidi, Nanoparticles in reverse osmosis membranes for desalination: A state of the art review, Desalination 475 (2020) 114171.

[54] J. Yin, B. Deng, Polymer-matrix nanocomposite membranes for water treatment, J. Membr. Sci. 479 (2015) 256-275.

[55] S.J. Gao, Y.Z. Zhu, Y.Q. Gong, Z.Y. Wang, W.X. Fang, J. Jin, Ultrathin Polyamide Nanofiltration Membrane Fabricated on Brush-Painted Single-Walled Carbon Nanotube Network Support for Ion Sieving, ACS Nano 13 (2019) 5278-5290.

[56] C.Y. Tang, Z. Yang, H. Guo, J.J. Wen, L.D. Nghiem, E. Cornelissen, Potable Water Reuse through Advanced Membrane Technology, Environ. Sci. Technol. 52 (2018) 10215-10223.

[57] A.F. Ismail, M. Padaki, N. Hilal, T. Matsuura, W.J. Lau, Thin film composite membrane — Recent development and future potential, Desalination 356 (2015) 140-148.

[58] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination-Development to date and future potential, J. Membr. Sci. 370 (2011) 1-22.

[59] H.S. Lee, S.J. Im, J.H. Kim, H.J. Kim, J.P. Kim, B.R. Min, Polyamide thin-film nanofiltration membranes containing TiO2 nanoparticles, Desalination 219 (2008) 48-56.

[60] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: Opportunities and challenges, J. Membr. Sci. 396 (2012) 1-21.

[61] X. Li, C.H. Loh, R. Wang, W. Widjajanti, J. Torres, Fabrication of a robust high-performance FO membrane by optimizing substrate structure and incorporating aquaporin into selective layer, J. Membr. Sci. 525 (2017) 257-268.

[62] Z. Alihemati, S.A. Hashemifard, T. Matsuura, A.F. Ismail, N. Hilal, Current status and challenges of fabricating thin film composite forward osmosis membrane: A comprehensive roadmap, Desalination 491 (2020) 114557.

[63] R.V. Linares, Z. Li, S. Sarp, S.S. Bucs, G. Amy, J.S. Vrouwenvelder, Forward osmosis niches in seawater desalination and wastewater reuse, Water Res. 66 (2014) 122-139.

[64] X. Wu, M. Ding, H. Xu, W. Yang, K. Zhang, H. Tian, H. Wang, Z. Xie, Scalable $Ti_3C_2T_x$ MXene Interlayered Forward Osmosis Membranes for Enhanced Water Purification and Organic Solvent Recovery, ACS Nano 14 (2020) 9125-9135.

[65] R.V. Linares, Z. Li, V. Yangali-Quintanilla, N. Ghaffour, G. Amy, T. Leiknes, J.S. Vrouwenvelder, Life cycle cost of a hybrid forward osmosis low pressure reverse osmosis system for seawater desalination and wastewater recovery, Water Res. 88 (2016) 225-234.

[66] N. Ma, J. Wei, R. Liao, C.Y. Tang, Zeolite-polyamide thin film nanocomposite membranes: Towards enhanced performance for forward osmosis, J. Membr. Sci. 405 (2012) 149-157.

[67] M.L. Lind, D.E. Suk, T.-V. Nguyen, E.M.V. Hoek, Tailoring the Structure of Thin Film Nanocomposite Membranes to Achieve Seawater RD Membrane Performance, Environ. Sci. Technol. 44 (2010) 8230-8235.

[68] P. Vandezande, L.E.M. Gevers, I.F.J. Vankelecom, Solvent resistant nanofiltration: separating on a molecular level, Chem. Soc. Rev. 37 (2008) 365-405.

[69] S. Darvishmanesh, L. Firoozpour, J. Vanneste, P. Luis, J. Degreve, B. Van der Bruggen,

Performance of solvent resistant nanofiltration membranes for purification of residual solvent in the pharmaceutical industry: experiments and simulation, Green Chem. 13 (2011) 3476-3483.

[70] S.-P. Sun, T.-S. Chung, K.-J. Lu, S.-Y. Chan, Enhancement of Flux and Solvent Stability of Matrimid (R) Thin-Film Composite Membranes for Organic Solvent Nanofiltration, AICHE J. 60 (2014) 3623-3633.

[71] Y. Li, Z. Guo, S. Li, B. Van der Bruggen, Interfacially Polymerized Thin-Film Composite Membranes for Organic Solvent Nanofiltration, Adv. Mater. Interfaces 8 (2021) 2001671.

[72] Y. Cui, T.-S. Chung, Pharmaceutical concentration using organic solvent forward osmosis for solvent recovery, Nat. Commun. 9 (2018) 1426.

[73] S. Bano, A. Mahmood, S.-J. Kim, K.-H. Lee, Graphene oxide modified polyamide nanofiltration membrane with improved flux and antifouling properties, J. Mater. Chem. A 3 (2015) 2065-2071.

[74] H. Wu, H. Sun, W. Hong, L. Mao, Y. Liu, Improvement of Polyamide Thin Film Nanocomposite Membrane Assisted by Tannic Acid-Fe-III Functionalized Multiwall Carbon Nanotubes, ACS Appl. Mater. Interfaces 9 (2017) 32255-32263.

[75] H. Dong, L. Zhao, L. Zhang, H. Chen, C. Gao, W.S. Winston Ho, High-flux reverse osmosis membranes incorporated with NaY zeolite nanoparticles for brackish water desalination, J. Membr. Sci. 476 (2015) 373-383.

[76] M. Zargar, Y. Hartanto, B. Jin, S. Dai, Understanding functionalized silica nanoparticles incorporation in thin film composite membranes: Interactions and desalination performance, J. Membr. Sci. 521 (2017) 53-64.

[77] H. Zhang, X.-Y. Gong, W.-X. Li, X.-H. Ma, C.Y. Tang, Z.-L. Xu, Thin-film nanocomposite membranes containing tannic acid-Fe^{3+} modified MoS_2 nanosheets with enhanced nanofiltration performance, J. Membr. Sci. 616 (2020) 118605.

[78] Z. Jiang, S. Karan, A.G. Livingston, Water Transport through Ultrathin Polyamide Nanofilms Used for Reverse Osmosis, Adv. Mater. 30 (2018) 1705973.

[79] H. Peng, W.-H. Zhang, W.-S. Hung, N. Wang, J. Sun, K.-R. Lee, Q.-F. An, C.-M. Liu, Q. Zhao, Phosphonium Modification Leads to Ultrapermeable Antibacterial Polyamide Composite Membranes with Unreduced Thickness, Adv. Mater. 32 (2020) 2001383.

[80] X.-H. Ma, Z.-K. Yao, Z. Yang, H. Guo, Z.-L. Xu, C.Y. Tang, M. Elimelech, Nanofoaming of Polyamide Desalination Membranes To Tune Permeability and Selectivity, Environ. Sci. Technol. Lett. 5 (2018) 123-130.

[81] Y.-L. Ji, Q.-F. An, Y.-S. Guo, W.-S. Hung, K.-R. Lee, C.-J. Gao, Bio-inspired fabrication of high perm-selectivity and anti-fouling membranes based on zwitterionic polyelectrolyte nanoparticles, J. Mater. Chem. A 4 (2016) 4224-4231.

[82] Y.-L. Ji, Q.-F. An, X.-D. Weng, W.-S. Hung, K.-R. Lee, C.-J. Gao, Microstructure and performance of zwitterionic polymeric nanoparticle/polyamide thin-film nanocomposite membranes for salts/organics separation, J. Membr. Sci. 548 (2018) 559-571.

[83] Y.-L. Ji, W.-J. Qian, Q.-F. An, S.-H. Huang, K.-R. Lee, C.-J. Gao, Mussel-inspired zwitterionic dopamine nanoparticles as building blocks for constructing salt selective nanocomposite membranes, J. Membr. Sci. 572 (2019) 140-151.

[84] C. Li, S. Li, L. Tian, J. Zhang, B. Su, M.Z. Hu, Covalent organic frameworks (COFs)-incorporated thin film nanocomposite (TFN) membranes for high-flux organic solvent nanofiltration (OSN), J. Membr. Sci. 572 (2019) 520-531.

[85] S. Feng, Z.-X. Low, S. Liu, L. Zhang, X. Zhang, G.P. Simon, X.-Y. Fang, H. Wang, Microporous

polymer incorporated polyamide membrane for reverse osmosis desalination, J. Membr. Sci. 610 (2020) 118299.

[86] F. Asempour, D. Emadzadeh, T. Matsuura, B. Kruczek, Synthesis and characterization of novel Cellulose Nanocrystals-based Thin Film Nanocomposite membranes for reverse osmosis applications, Desalination 439 (2018) 179-187.

[87] L. Xu, B. Shan, C. Gao, J. Xu, Multifunctional thin-film nanocomposite membranes comprising covalent organic nanosheets with high crystallinity for efficient reverse osmosis desalination, J. Membr. Sci. 593 (2020) 117398.

[88] Z. Sung, Q. Wu, C. Ye, W. Wang, L. Zheng, F. Dong, Z. Yi, L. Xue, C. Gao, Nanovoid Membranes Embedded with Hollow Zwitterionic Nanocapsules for a Superior Desalination Performance, Nano Lett. 19 (2019) 2953-2959.

[89] C. Wang, Z. Li, J. Chen, Z. Li, Y. Yin, L. Cao, Y. Zhong, H. Wu, Covalent organic framework modified polyamide nanofiltration membrane with enhanced performance for desalination, J. Membr. Sci. 523 (2017) 273-281.

[90] D. Klemm, F. Kramer, S. Moritz, T. Lindstrom, M. Ankerfors, D. Gray, A. Dorris, Nanocelluloses: A New Family of Nature-Based Materials, Angew. Chem. Int. Edit. 50 (2011) 5438-5466.

[91] R.J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, Cellulose nanomaterials review: structure, properties and nanocomposites, Chem. Soc. Rev. 40 (2011) 3941-3994.

[92] B.L. Peng, N. Dhar, H.L. Liu, K.C. Tam, Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective, Can. J. Chem. Eng. 89 (2011) 1191-1206.

[93] L. Bai, N. Bossa, F. Qu, J. Winglee, G. Li, K. Sun, H. Liang, M.R. Wiesner, Comparison of Hydrophilicity and Mechanical Properties of Nanocomposite Membranes with Cellulose Nanocrystals and Carbon Nanotubes, Environ. Sci. Technol. 51 (2017) 253-262.

[94] P. Cruz-Tato, E.O. Ortiz-Quiles, K. Vega-Figueroa, L. Santiago-Martoral, M. Flynn, L.M. Díaz-Vázquez, E. Nicolau, Metalized Nanocellulose Composites as a Feasible Material for Membrane Supports: Design and Applications for Water Treatment, Environ. Sci. Technol. 51 (2017) 4585-4595.

[95] D. Zhang, A. Karkooti, L. Liu, M. Sadrzadeh, T. Thundat, Y. Liu, R. Narain, Fabrication of antifouling and antibacterial polyethersulfone (PES)/cellulose nanocrystals (CNC) nanocomposite membranes, J. Membr. Sci. 549 (2018) 350-356.

[96] Y. Liu, L. Bai, X. Zhu, D. Xu, G. Li, H. Liang, M.R. Wiesner, The role of carboxylated cellulose nanocrystals placement in the performance of thin-film composite (TFC) membrane, J. Membr. Sci. 617 (2021) 118581.

[97] M.T. Hoang, T.D. Pham, D. Verheyen, M.K. Nguyen, T.T. Pham, J. Zhu, B. Van der Bruggen, Fabrication of thin film nanocomposite nanofiltration membrane incorporated with cellulose nanocrystals for removal of Cu(II) and Pb(II), Chem. Eng. Sci. 228 (2020) 115998.

[98] Y. Habibi, L.A. Lucia, O.J. Rojas, Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications, Chem. Rev. 110 (2010) 3479-3500.

[99] S. Montanari, M. Roumani, L. Heux, M.R. Vignon, Topochemistry of Carboxylated Cellulose Nanocrystals Resulting from TEMPO-Mediated Oxidation, Macromolecules 38 (2005) 1665-1671.

[100] S.H. Kim, S.Y. Kwak, T. Suzuki, Positron annihilation spectroscopic evidence to demonstrate the flux-enhancement mechanism in morphology-controlled thin-film-composite (TFC) membrane, Environ. Sci. Technol. 39 (2005) 1764-1770.

[101] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-inspired surface chemistry for multifunctional coatings, Science 318 (2007) 426-430.

[102] H.-C. Yang, K.-J. Liao, H. Huang, Q.-Y. Wu, L.-S. Wan, Z.-K. Xu, Mussel-inspired modification of a polymer membrane for ultra-high water permeability and oil-in-water emulsion separation, J. Mater. Chem. A 2 (2014) 10225-10230.

[103] K. Cheng, N. Zhang, N. Yang, S. Hou, J. Ma, L. Zhang, Y. Sun, B. Jiang, Rapid and robust modification of PVDF ultrafiltration membranes with enhanced permselectivity, antifouling and antibacterial performance, Sep. Purif. Technol. 262 (2021) 118316.

[104] Y. Zhang, J. Ma, L. Shao, Ultra-thin trinity coating enabled by competitive reactions for unparalleled molecular separation, J. Mater. Chem. A 8 (2020) 5078-5085.

[105] S. Xiong, Y. Wang, J. Yu, L. Chen, J. Zhu, Z. Hu, Polydopamine particles for next-generation multifunctional biocomposites, J. Mater. Chem. A 2 (2014) 7578-7587.

[106] X. Song, Y. Zhang, Y. Wang, M. Huang, S. Gul, H. Jiang, Nanocomposite membranes embedded with dopamine-melanin nanospheres for enhanced interfacial compatibility and nanofiltration performance, Sep. Purif. Technol. 242 (2020) 116816.

[107] Z. Wang, H.-C. Yang, F. He, S. Peng, Y. Li, L. Shao, S.B. Darling, Mussel-Inspired Surface Engineering for Water-Remediation Materials, Matter 1 (2019) 115-155.

[108] M. Kumar, M. Grzelakowski, J. Zilles, M. Clark, W. Meier, Highly permeable polymeric membranes based on the incorporation of the functional water channel protein Aquaporin Z, P. Natl. Acad. SCI. USA 104 (2007) 20719-20724.

[109] K. Murata, K. Mitsuoka, T. Hirai, T. Walz, P. Agre, J.B. Heymann, A. Engel, Y. Fujiyoshi, Structural determinants of water permeation through aquaporin-1, Nature 407 (2000) 599-605.

[110] S. Qi, R. Wang, G.K.M. Chaitra, J. Torres, X. Hu, A.G. Fane, Aquaporin-based biomimetic reverse osmosis membranes: Stability and long term performance, J. Membr. Sci. 508 (2016) 94-103.

[111] X. Li, S. Chou, R. Wang, L. Shi, W. Fang, G. Chaitra, C.Y. Tang, J. Torres, X. Hu, A.G. Fane, Nature gives the best solution for desalination: Aquaporin-based hollow fiber composite membrane with superior performance, J. Membr. Sci. 494 (2015) 68-77.

[112] Z. Li, R.V. Linares, S. Bucs, L. Fortunato, C. Helix-Nielsen, J.S. Vrouwenvelder, N. Ghaffour, T. Leiknes, G. Amy, Aquaporin based biomimetic membrane in forward osmosis: Chemical cleaning resistance and practical operation, Desalination 420 (2017) 208-215.

[113] H. Huang, S. Lin, L. Zhang, L.a. Hou, Chlorine-Resistant Polyamide Reverse Osmosis Membrane with Monitorable and Regenerative Sacrificial Layers, ACS Appl. Mater. Interfaces 9 (2017) 10214-10223.

[114] A.P. Cote, A.I. Benin, N.W. Ockwig, M. O'Keeffe, A.J. Matzger, O.M. Yaghi, Porous, crystalline, covalent organic frameworks, Science 310 (2005) 1166-1170.

[115] H. Yang, L. Yang, H. Wang, Z. Xu, Y. Zhao, Y. Luo, N. Nasir, Y. Song, H. Wu, F. Pan, Z. Jiang, Covalent organic framework membranes through a mixed-dimensional assembly for molecular separations, Nat. Commun. 10 (2019) 2101.

[116] L. Valentino, M. Matsumoto, W.R. Dichtel, B.J. Mariñas, Development and Performance Characterization of a Polyimine Covalent Organic Framework Thin-Film Composite Nanofiltration Membrane, Environ. Sci. Technol. 51 (2017) 14352-14359.

[117] X. Cao, Z. Qiao, Z. Wang, S. Zhao, P. Li, J. Wang, S. Wang, Enhanced performance of mixed matrix membrane by incorporating a highly compatible covalent organic framework into poly(vinylamine) for hydrogen purification, Int. J. Hydrogen Energy 41 (2016) 9167-9174.

[118] S. Yuan, X. Li, J. Zhu, G. Zhang, P. Van Puyvelde, B. Van der Bruggen, Covalent organic frameworks for membrane separation, Chem. Soc. Rev. 48 (2019) 2665-2681.

[119] X. Ma, Y. Zhao, Biomedical Applications of Supramolecular Systems Based on Host-Guest Interactions, Chem. Rev. 115 (2015) 7794-7839.

[120] J.S. Kim, D.T. Quang, Calixarene-derived fluorescent probes, Chem. Rev. 107 (2007) 3780-3799.

[121] J. Wu, J. Liu, T.-S. Chung, Structural Tuning of Polymers of Intrinsic Microporosity via the Copolymerization with Macrocyclic 4-tert-butylcalix 4 arene for Enhanced Gas Separation Performance, Adv. Sustain. Syst. 2 (2018) 1800044.

[122] H.-C.J. Zhou, S. Kitagawa, Metal-Organic Frameworks (MOFs), Chem. Soc. Rev. 43 (2014) 5415-5418.

[123] H.-C. Zhou, J.R. Long, O.M. Yaghi, Introduction to Metal-Organic Frameworks, Chem. Rev. 112 (2012) 673-674.

[124] C. Echaide-Gorriz, S. Sorribas, C. Tellez, J. Coronas, MOF nanoparticles of MIL-68(Al), MIL-101(Cr) and ZIF-11 for thin film nanocomposite organic solvent nanofiltration membranes, RSC Adv. 6 (2016) 90417-90426.

[125] C. Echaide-Gorriz, M. Navarro, C. Tellez, J. Coronas, Simultaneous use of MOFs MIL-101(Cr) and ZIF-11 in thin film nanocomposite membranes for organic solvent nanofiltration, Dalton T. 46 (2017) 6244-6252.

[126] Y. Zhang, X. Cheng, X. Jiang, J.J. Urban, C.H. Lau, S. Liu, L. Shao, Robust natural nanocomposites realizing unprecedented ultrafast precise molecular separations, Mater. Today 36 (2020) 40-47.

[127] X. Guo, D. Liu, T. Han, H. Huang, Q. Yang, C. Zhong, Preparation of Thin Film Nanocomposite Membranes with Surface Modified MOF for High Flux Organic Solvent Nanofiltration, AICHE J. 63 (2017) 1303-1312.

[128] J. Duan, Y. Pan, F. Pacheco, E. Litwiller, Z. Lai, I. Pinnau, High-performance polyamide thin-film-nanocomposite reverse osmosis membranes containing hydrophobic zeolitic imidazolate framework-8, J. Membr. Sci. 476 (2015) 303-310.

[129] Z. Hu, Y. Chen, J. Jiang, Zeolitic imidazolate framework-8 as a reverse osmosis membrane for water desalination: Insight from molecular simulation, J. Chem. Phys. 134 (2011) 134705.

[130] J.K. Holt, H.G. Park, Y.M. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, A. Noy, O. Bakajin, Fast mass transport through sub-2-nanometer carbon nanotubes, Science 312 (2006) 1034-1037.

[131] S. Turgman-Cohen, J.C. Araque, E.M.V. Hoek, F.A. Escobedo, Molecular Dynamics of Equilibrium and Pressure-Driven Transport Properties of Water through LTA-Type Zeolites, Langmuir 29 (2013) 12389-12399.

[132] J. Zhu, L. Qin, A. Uliana, J. Hou, J. Wang, Y. Zhang, X. Li, S. Yuan, J. Li, M. Tian, J. Lin, B. Van der Bruggen, Elevated Performance of Thin Film Nanocomposite Membranes Enabled by Modified Hydrophilic MOFs for Nanofiltration, ACS Appl. Mater. Interfaces 9 (2017) 1975-1986.

[133] Y. Xu, X. Gao, X. Wang, Q. Wang, Z. Ji, X. Wang, T. Wu, C. Gao, Highly and Stably Water Permeable Thin Film Nanocomposite Membranes Doped with MIL-101 (Cr) Nanoparticles for Reverse Osmosis Application, Materials 9 (2016) 870.

[134] J.H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K.P. Lillerud, A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability, J. Am. Chem. Soc. 130 (2008) 13850-13851.

[135] X. Liu, N.K. Demir, Z. Wu, K. Li, Highly Water-Stable Zirconium Metal Organic Framework UiO-66 Membranes Supported on Alumina Hollow Fibers for Desalination, J. Am. Chem. Soc. 137

(2015) 6999-7002.

[136] Z. Hu, D. Zhao, De facto methodologies toward the synthesis and scale-up production of UiO-66-type metal-organic frameworks and membrane materials, Dalton T. 44 (2015) 19018-19040.

[137] Q. Li, Z. Liao, J. Xie, L. Ni, C. Wang, J. Qi, X. Sun, L. Wang, J. Li, Enhancing nanofiltration performance by incorporating tannic acid modified metal-organic frameworks into thin-film nanocomposite membrane, Environmental Research 191 (2020) 110215.

[138] L. Liu, X. Xie, S. Qi, R. Li, X. Zhang, X. Song, C. Gao, Thin film nanocomposite reverse osmosis membrane incorporated with UiO-66 nanoparticles for enhanced boron removal, J. Membr. Sci. 580 (2019) 101-109.

[139] Y.P. Tang, L. Luo, Z. Thong, T.S. Chung, Recent advances in membrane materials and technologies for boron removal, J. Membr. Sci. 541 (2017) 434-446.

[140] J. Wang, Y. Wang, Y. Zhang, A. Uliana, J. Zhu, J. Liu, B. Van der Bruggen, Zeolitic Imidazolate Framework/Graphene Oxide Hybrid Nanosheets Functionalized Thin Film Nanocomposite Membrane for Enhanced Antimicrobial Performance, ACS Appl. Mater. Interfaces 8 (2016) 25508-25519.

[141] C. Van Goethem, R. Verbeke, S. Hermans, R. Bernstein, I.F.J. Vankelecom, Controlled positioning of MOFs in interfacially polymerized thin-film nanocomposites, J. Mater. Chem. A 4 (2016) 16368-16376.

[142] M. Navarro, J. Benito, L. Paseta, I. Gascon, J. Coronas, C. Tellez, Thin-Film Nanocomposite Membrane with the Minimum Amount of MOF by the Langmuir-Schaefer Technique for Nanofiltration, ACS Appl. Mater. Interfaces 10 (2018) 1278-1287.

[143] L. Wang, M. Fang, J. Liu, J. He, J. Li, J. Lei, Layer-by-Layer Fabrication of High-Performance Polyamide/ZIF-8 Nanocomposite Membrane for Nanofiltration Applications, ACS Appl. Mater. Interfaces 7 (2015) 24082-24093.

[144] L. Sarango, L. Paseta, M. Navarro, B. Zornoza, J. Coronas, Controlled deposition of MOFs by dip-coating in thin film nanocomposite membranes for organic solvent nanofiltration, J, Ind. Eng. Chem. 59 (2018) 8-16.

[145] J. Zhu, J. Hou, S. Yuan, Y. Zhao, Y. Li, R. Zhang, M. Tian, J. Li, J. Wang, B. Van der Bruggen, MOF-positioned polyamide membranes with a fishnet-like structure for elevated nanofiltration performance, J. Mater. Chem. A 7 (2019) 16313-16322.

[146] C. Van Goethem, R. Verbeke, M. Pfanmoeller, T. Koschine, M. Dickmann, T. Timpel-Lindner, W. Egger, S. Bals, I.F.J. Vankelecom, The role of MOFs in Thin-Film Nanocomposite (TFN) membranes, J. Membr. Sci. 563 (2018) 938-948.

[147] M.L. Lind, B.-H. Jeong, A. Subramani, X. Huang, E.M.V. Hoek, Effect of mobile cation on zeolite-polyamide thin film nanocomposite membranes, J. Mater. Res. 24 (2009) 1624-1631.

[148] F. Yang, H. Sadam, Y. Zhang, J. Xia, X. Yang, J. Long, S. Li, L. Shao, A de novo sacrificial-MOF strategy to construct enhanced-flux nanofiltration membranes for efficient dye removal, Chem. Eng. Sci. 225 (2020) 115845.

[149] J.-J. Wang, H.-C. Yang, M.-B. Wu, X. Zhang, Z.-K. Xu, Nanofiltration membranes with cellulose nanocrystals as an interlayer for unprecedented performance, J. Mater. Chem. A 5 (2017) 16289-16295.

[150] Y. Hao, Q. Li, B. He, B. Liao, X. Li, M. Hu, Y. Ji, Z. Cui, M. Younas, J. Li, An ultrahighly permeable-selective nanofiltration membrane mediated by an in situ formed interlayer, J. Mater. Chem. A 8 (2020) 5275-5283.

[151] Y. Zhu, W. Xie, S. Gao, F. Zhang, W. Zhang, Z. Liu, J. Jin, Single-Walled Carbon Nanotube Film Supported Nanofiltration Membrane with a Nearly 10 nm Thick Polyamide Selective Layer for

High-Flux and High-Rejection Desalination, Small 12 (2016) 5034-5041.

[152] J. Wang, J. Zhu, Y. Zhang, J. Liu, B. Van der Bruggen, Nanoscale tailor-made membranes for precise and rapid molecular sieve separation, Nanoscale 9 (2017) 2942-2957.

[153] Y. Liang, Y. Zhu, C. Liu, K.-R. Lee, W.-S. Hung, Z. Wang, Y. Li, M. Elimelech, J. Jin, S. Lin, Polyamide nanofiltration membrane with highly uniform sub-nanometre pores for sub-1A precision separation, Nat. Commun. 11 (2020) 2015-2015.

[154] V. Kolev, V. Freger, Hydration, porosity and water dynamics in the polyamide layer of reverse osmosis membranes: A molecular dynamics study, Polymer 55 (2014) 1420-1426.

[155] Z. Yang, Y. Wu, H. Guo, X.-H. Ma, C.-E. Lin, Y. Zhou, B. Cao, B.-K. Zhu, K. Shih, C.Y. Tang, A novel thin-film nano-templated composite membrane with in situ silver nanoparticles loading: Separation performance enhancement and implications, J. Membr. Sci. 544 (2017) 351-358.

[156] D.M. Stevens, J.Y. Shu, M. Reichert, A. Roy, Next-Generation Nanoporous Materials: Progress and Prospects for Reverse Osmosis and Nanofiltration, Ind. Eng. Chem. Res. 56 (2017) 10526-10551.

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