

1 **A Critical Review on Thin-film Nanocomposite Membranes with**
2 **Interlayered Structure: Mechanisms, Recent Developments, and**
3 **Environmental Applications**

4
5 Zhe Yang,^{*,†,1} Peng-Fei Sun,^{†,‡,1} Xianhui Li,[§] Bowen Gan,^{†,||} Li Wang,[†] Xiaoxiao Song,^{||}
6 Hee-Deung Park,[‡] and Chuyang Y. Tang^{*,†}

7 [†]Department of Civil Engineering, The University of Hong Kong, Pokfulam, Hong Kong

8 [‡]School of Civil, Environmental and Architectural Engineering, Korea University, Seoul,
9 02841, South Korea

10 [§]Key Laboratory for City Cluster Environmental Safety and Green Development of the
11 Ministry of Education, Institute of Environmental and Ecological Engineering,
12 Guangdong University of Technology, Guangzhou, 510006, China

13 ^{||}Centre for Membrane and Water Science & Technology, Ocean College, Zhejiang
14 University of Technology, Hangzhou, 310014, P. R. China

15

16 ^{*}To whom all correspondence should be addressed.

17 Tel: +852 2859 1976, E-mail address: tangc@hku.hk

18 Tel: +852 2857 8470, E-mail address: zheyang@connect.hku.hk

19

20 **Author Contributions**

21 ¹These authors contributed equally to this work.

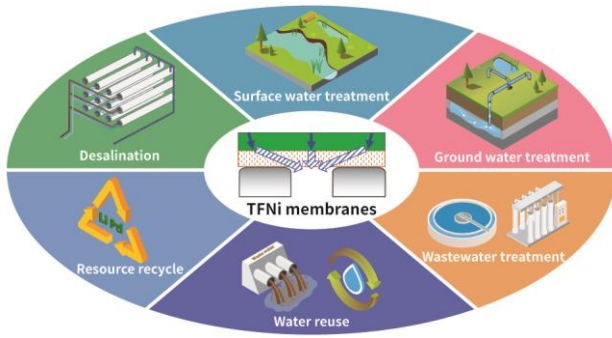
22

23 **ABSTRACT**

24 The separation properties of polyamide reverse osmosis and nanofiltration membranes,
25 widely applied for desalination and water reuse, are constrained by the
26 permeability-selectivity upper bound. Although thin-film nanocomposite (TFN) membranes
27 incorporating nanomaterials exhibit enhanced water permeance, their rejection is only
28 moderately improved or even impaired due to agglomeration of nanomaterials and formation
29 of defects. A novel type of TFN membranes featuring an interlayer of nanomaterials (TFNi)
30 has emerged in recent years. These novel TFNi membranes show extraordinary improvement
31 in water flux (e.g., up to an order of magnitude enhancement) along with better selectivity.
32 Such enhancements can be achieved by a wide selection of nanomaterials, ranging from
33 nanoparticles, one-/two-dimensional materials to interfacial coatings. The use of
34 nano-structured interlayers not only improve the formation of polyamide rejection layers but
35 also provide an optimized water transport path, which enables TFNi membranes to
36 potentially overcome the longstanding tradeoff between membrane permeability and
37 selectivity. Furthermore, TFNi membranes can potentially enhance the removal of heavy
38 metals and micropollutants, which is critical for many environmental applications. This
39 review critically examines the recent developments of TFNi membranes and discusses the
40 underlying mechanisms and design criteria. Their potential environmental applications are
41 also highlighted.

42

43 TOC



44

45 ■ INTRODUCTION

46 Global water scarcity has been recognized as one of the most critical challenges in the new
47 millennium,¹⁻³ and it has been estimated that half of the world's population will be living in
48 water-stressed regions by 2025.⁴ Membrane-based separation technologies, such as reverse
49 osmosis (RO) and nanofiltration (NF), play increasingly important roles in efficient water
50 production, reuse, and desalination.^{2, 5-7} RO and NF membranes used for seawater
51 desalination and water reuse generally have a thin-film composite (TFC) structure that
52 consists of an ultra-thin polyamide selective layer of approximately 10-400 nm in thickness
53 supported by a porous substrate.^{5, 6} TFC membranes are formed by an interfacial
54 polymerization (IP) reaction, typically between *m*-phenylenediamine (MPD) or piperazine
55 (PIP) in an aqueous phase with trimesoyl chloride (TMC) in an organic phase. These
56 membranes have a wide range of operating pHs (e.g., pH 2-11) and reasonable thermal
57 stability (up to 60 °C).^{8,9} Unfortunately, their separation performances are constrained by a
58 permeability-selectivity trade-off known as the “upper bound”.¹⁰⁻¹² Consequently, TFC
59 membranes often have relatively low water permeance (1-20 L m⁻²h⁻¹bar⁻¹) in order to
60 maintain the desired selectivity.¹⁰ Moreover, membrane fouling and susceptibility to chlorine
61 attack are major issues that can deteriorate membrane integrity, decrease its life span and/or
62 increase maintenance cost.^{13, 14} These limitations of TFC membranes motivate membrane
63 scientists to develop next-generation high-performance RO and NF membranes.^{6, 12, 15, 16}

64

65 Over the past decade, TFC membranes incorporating nanomaterials have been extensively
66 studied (Figure 1). This approach has been shown to successfully enhance water
67 permeance¹⁷⁻²⁶ and improve anti(bio)fouling properties.²⁴⁻³⁵ Nanomaterials can be
68 incorporated into polyamide rejection layers by adding them in the monomer (MPD or TMC)
69 solutions to prepare thin-film nanocomposite membranes (TFN, Figure 1a).^{16, 36} Alternatively,
70 they can be added into the substrate to prepare thin-film composite membranes with a
71 nanocomposite substrate (TFCn, Figure 1b).⁶ Hoek and coworkers¹⁷ pioneered the concept of
72 TFN in 2007 by incorporating porous zeolite nanoparticles (NPs) of 0.4 nm internal pores in

73 the polyamide rejection layer of an RO membrane. The resulting membrane showed an
74 enhancement of 81% in water permeance with nearly unchanged salt rejection compared to
75 the unmodified membrane. Various other nanomaterials, such as silica, TiO₂,
76 metal-organic-frameworks (MOFs), and Ag, have also been reported for TFN membranes.^{16,}
77 ^{37, 38} In parallel, Pendergast et al.^{39, 40} incorporated silica and zeolite nanoparticles into a
78 polysulfone (PSF) substrate to fabricate TFCn membrane with higher water permeance and
79 improved mechanical stability. Likewise, Ma et al.⁴¹ demonstrated improved water
80 permeance and reduced internal concentration polarization for a TFCn forward osmosis (FO)
81 membrane with hydrophilic and porous zeolite nanoparticles loaded in its substrate. These
82 works have been followed by a slate of additional investigations reporting the use of other
83 nanomaterials, such as TiO₂,⁴² carbon nanotubes (CNTs)⁴³⁻⁴⁵ and graphene oxide (GO).⁴⁶
84 Several TFN membranes have also been successfully commercialized.⁴⁷⁻⁴⁹ Figure 2 presents
85 the performance enhancement factors in terms of water permeance (*A* value) and water/salt
86 selectivity (*A/B*) for TFN and TFCn membranes reported in the recent literature. The majority
87 of these membranes have up to 200% enhancement in water permeance. Nevertheless,
88 enhancement in selectivity *A/B* is far less obvious, with many membranes even suffering
89 from compromised selectivity due to the aggregation of nanomaterials or impaired polyamide
90 integrity.^{16, 46, 50-54}

91

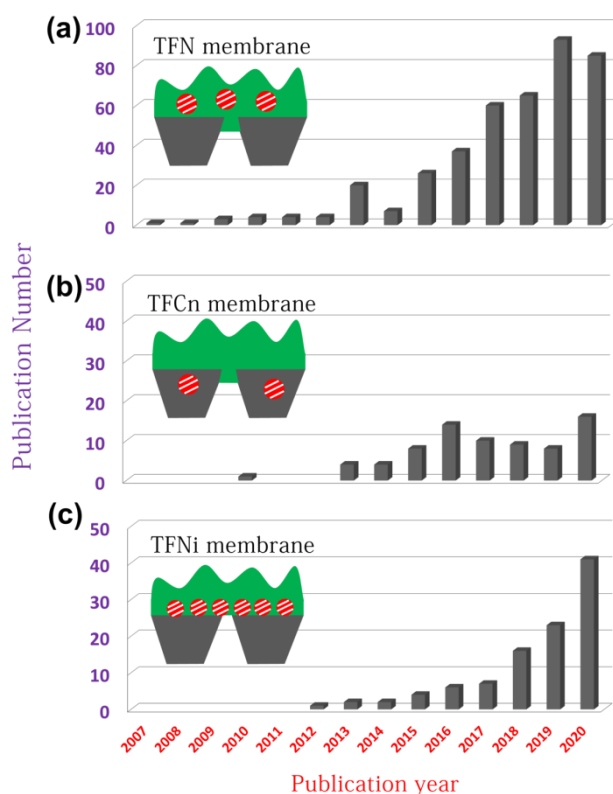
92 Growing interests have been focused on fabricating thin-film nanocomposite membranes with
93 an interlayer (TFNi), where nanomaterials or coating layers can be uniformly deposited on
94 the substrate before forming the polyamide layer. In 2015, Karan et al.⁵⁵ fabricated TFNi
95 membranes *via* introducing a sacrificial layer of cadmium hydroxide nanostrands for
96 controlling the rate of IP reaction. They demonstrated a TFNi membrane with two orders of
97 magnitude higher water flux than that of commercial membranes. A slate of other
98 nanomaterials, from nanoparticles (e.g., TiO₂,⁵⁶ Ag⁵⁷), 1D (e.g., CNTs⁵⁸⁻⁶⁰), and 2D (e.g.,
99 GO^{61, 62} and MOFs⁶³⁻⁶⁶) materials to other interfacial coating materials (e.g., polydopamine⁶⁷
100 and polyelectrolytes⁶⁸), have also been reported for making TFNi membranes based on

101 surface coating,⁶⁷ covalent bonding,⁶⁹ co-deposition,⁷⁰ *in situ* growth,⁷¹ evaporation,⁶⁵ etc..⁵⁹

102 Despite the growing number of publications on TFNi membranes (Figure 1c) and their
103 dramatically enhanced separation performance (Figure 2), a critical review of TFNi
104 membranes and their potential applications is not yet available.

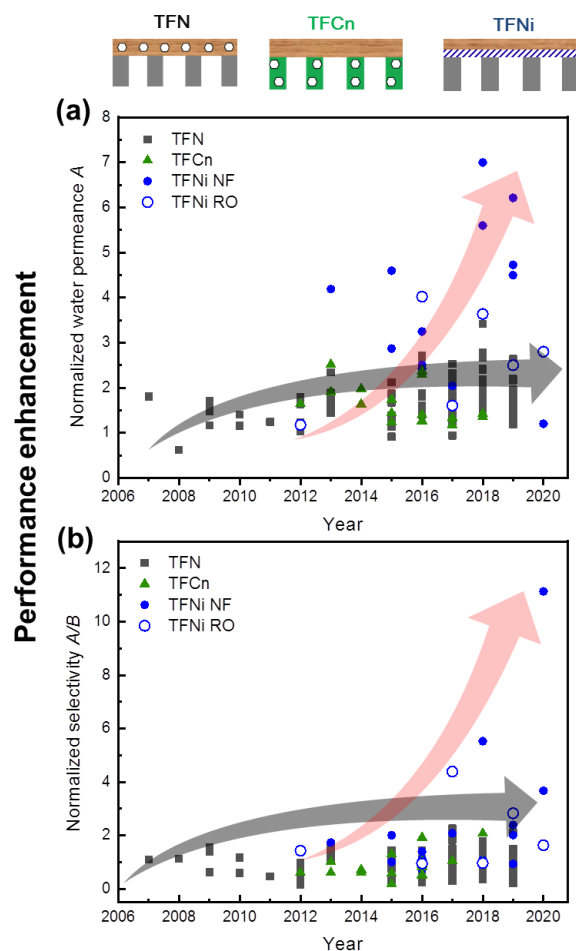
105

106 This paper provides a comprehensive review of the recent development of TFNi RO and NF
107 membranes. The mechanisms responsible for their enhanced water transport and solute
108 rejection are critically analyzed. The methods and design principles for high-performance
109 TFNi membranes are highlighted, and their environmental applications are systematically
110 assessed.



111

112 **Figure 1.** Recent publications of TFN, TFCn and TFNi membranes. Data for year 2020 is
113 incomplete. All data were obtained by searching the keyword “thin film nanocomposite
114 membrane” in the database of Scopus, with further manual screening to differentiate the types
115 of TFN, TFCn and TFNi membranes.



116

117 **Figure 2.** Performance enhancement factors of TFN, TFCn and TFNi (● symbol representing
 118 for NF and ○ representing for RO) over the recent years: (a) A value and (b) A/B value
 119 normalized by the respective values of the control TFC membrane without the inclusion of
 120 nanomaterials. The A/B values were based on simple salts (NaCl for RO membranes and
 121 Na₂SO₄ for NF membranes).

122

123 ■ CONVENTIONAL TFN AND TFCn MEMBRANES

124 While a comprehensive review of conventional TFN and TFCn membranes is beyond the
 125 scope of the current paper and can be found elsewhere,^{16, 37, 38, 72, 73} a brief discussion of these
 126 membranes and the relevant transport mechanisms are helpful to facilitate the better
 127 understanding of TFNi membranes. Table 1 classifies TFN and TFCn membranes based on
 128 the types of the incorporated nanofillers (e.g., solid, porous or sacrificial fillers). Solid
 129 nanofillers such as silica,^{50, 51, 53, 74} silver,⁷⁵ TiO₂^{76, 77}, ZnO⁷⁸ and 2D-nanoclay⁷⁹ have been
 130 shown to enhance the permeance of TFN membranes by improving their hydrophilicity¹⁶

131 and/or creating interfacial nanochannels between the nanofillers and the polyamide matrix.⁵⁷
132 ⁵⁸ In comparison, porous nanofillers such as microporous zeolite,^{17, 80} mesoporous silica,^{18, 54,}
133 ⁸¹ MOFs,^{23, 82-84} covalent-organic-frameworks (COFs),⁸⁵ aquaporins,⁸⁶⁻⁸⁸ and artificial water
134 channels⁸⁹ can provide additional selective water channels through their defined
135 micro/mesopores to further enhance separation performance.^{16, 17, 37, 73} Sacrificial nanofillers,
136 which are etched after membrane formation, can also be used to generate nanosized voids or
137 channels in the polyamide rejection layer to enhance its permeance.⁹⁰ Enhanced formation of
138 nanovoids of several tens of nm in size can also be achieved by the creation of nanosized gas
139 bubbles.⁹¹⁻⁹³

140

141 The solute rejection and thus selectivity of TFN membranes are strongly dependent on the
142 properties of the incorporated nanofillers.¹⁶ It is believed that highly defined interior channels
143 of some porous nanofillers (e.g., zeolite,¹⁷ MOFs,⁸³ COFs⁸⁵ and aquaporins⁹⁴) can
144 significantly enhance membrane selectivity due to their size exclusion effect.^{6, 7, 16, 37, 73} While
145 their nanochannels are large enough for the transport of water, a solute whose size is greater
146 than the channel size cannot transport through the interior channels. Solute rejection can also
147 be improved by additional solute-nanofiller interactions such as enhanced electrostatic
148 repulsion of anions by negatively charged nanofillers (e.g., silica,¹⁸ Ag,⁹⁵ GO⁵², and MOF⁹⁶).








149 Similarly, the use of some hydrophilic nanomaterials (e.g., polydopamine, hydrophilic MOFs,
150 etc.) has been shown to improve the selectivity against hydrophobic compounds such as
151 endocrine disruptor compounds (EDCs) as a result of suppressed hydrophobic interaction.⁹⁷⁻⁹⁹
152 In addition to interior channels, selective interfacial nanochannels can also be created to
153 achieve enhanced solute rejection.⁵⁷ Nevertheless, despite the presence of selective
154 nanochannels (i.e., interior channels for porous fillers and interfacial channels for both porous
155 and solid fillers), many TFN membranes show little enhancement in selectivity or even suffer
156 from reduced solute rejection (Figure 2b) as a result of impaired membrane integrity caused
157 by aggregations of NPs^{52, 54} and/or defects formation.⁵⁸ Compared to typical interior channels
158 and interfacial channels of sub-nm to a few nm, nanovoids or channels created by sacrificial



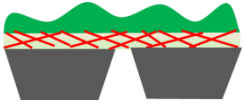


159 fillers often have much larger sizes (e.g., ~ or > 10 nm), making them less selective. For
160 example, Yang et al.⁹⁰ incorporated sacrificial copper nanoparticles (CuNPs) in a polyamide
161 rejection layer. The nanovoids resulted from the subsequent acid etching led to a 3-fold
162 increase in water flux but at the expense of slightly decrease NaCl rejection.

163

164 In a similar fashion, solid, porous and sacrificial nanofillers can be incorporated into the
165 support layer to prepare TFCn membranes (Table 1).^{43, 46, 51, 76, 100} Like TFN membranes,
166 TFCn membranes can achieve significant enhancement in membrane permeance but often
167 show similar or even reduced solute rejection compared to their respective controls without
168 the loading of nanofillers.^{51, 101} In addition to RO, TFCn membranes are often reported for
169 forward osmosis (FO) or pressure retarded osmosis (PRO), since the enhanced hydrophilicity
170 and porosity of the substrate is favorable to reduce the structural parameter (i.e., the *S* value)
171 and to mitigate internal concentration polarization (ICP).^{41, 43} Studies^{39, 40, 102} also reported
172 enhanced membrane mechanical stability for some TFCn membranes due to the interaction
173 between the nanofillers and the polymeric matrix of the substrate.

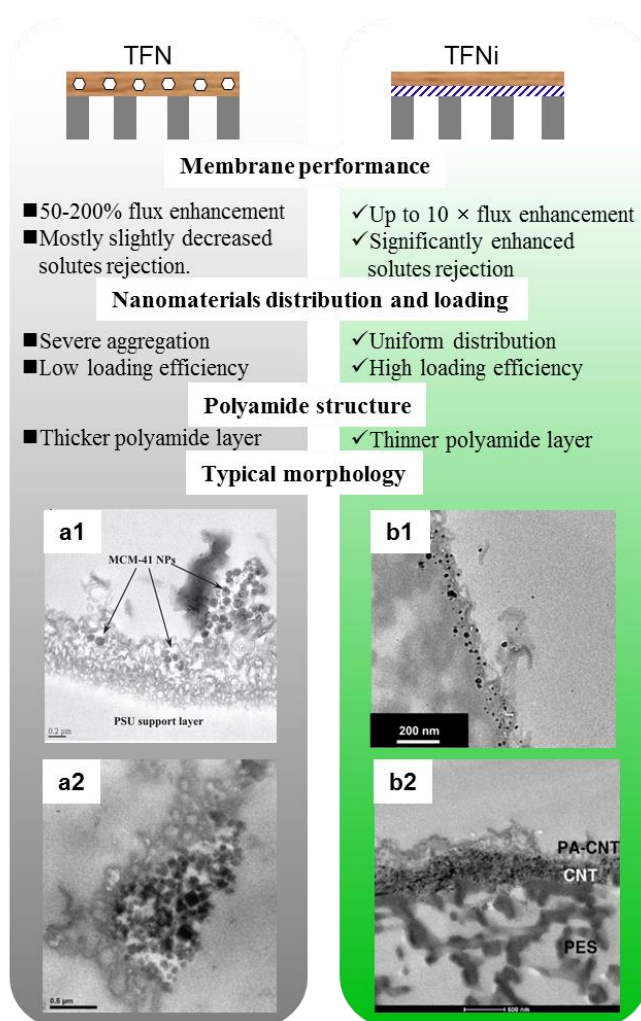
174 **Table 1.** Classifications of different nanocomposite membranes.

	Type of nanofillers	Membrane structure	Examples	Transport mechanism	General membrane performance
TFN	Solid fillers		ZnO, ¹⁰³ Ag, ⁹⁵ silica ^{104, 105} and TiO ₂ . ^{106, 107}	Nanofiller-induced interfacial channels; potentially improved selectivity due to enhanced size exclusion, hydrophilicity and/or charge repulsion	Enhancement of permeance by up to 200%. Despite the potential of selective interior and/or interfacial channels, TFN membranes often show no major improvements in solute rejection (or even deteriorated rejection) due to aggregations of NPs and/or formation of defects in the polyamide rejection layer.
	Porous fillers		Zeolite, ^{17, 80} MCM-41, ^{18, 54} CNT, ^{108, 109} MOFs, ^{82, 83} COFs, ⁸⁵ β-cyclodextrin, ¹¹⁰ and aquaporins. ^{86, 87}	Selective interior channels in addition to the possible presence of interfacial channels; potentially improved selectivity due to enhanced size exclusion, hydrophilicity and/or charge repulsion	
	Sacrificial fillers (Nanovoid formation)		Enhanced nanobubble formation. ⁹¹⁻⁹³	Relatively large (and non-selective) nanovoids of ~ or > 10 nm in size; enhanced water transport	
TFCn	Solid fillers		ZnO, ¹¹¹ Ag, ⁷⁵ silica ^{50, 74} and TiO ₂ . ¹¹²	Enhanced hydrophilicity of substrate	Enhanced permeance, often with similar or deteriorated solute rejection for RO membranes. Reduced S value and thus ICP for FO and PRO membranes.
	Porous fillers		Zeolite, ^{40, 41} MCM-41, ⁵¹ CNT ^{43, 113} and MOFs. ¹⁰¹	Improved porosity and/or hydrophilicity of substrate	
	Sacrificial fillers (Nanovoids)		Etching of MOF ¹⁰⁰ and CaCO ₃ . ¹¹⁴	Improved porosity of substrate	
TFNi	NPs, in the form of solid, porous and sacrificial nanofillers		TiO ₂ , ¹¹⁵ Ag ^{57, 71}	Mitigated NPs aggregation; enhanced hydrophilicity; additional water pathways and reduced membrane	Enhancement of water permeance by up to an order of magnitude with

			Zeolite, ¹¹⁶ MOFs ^{63, 64}	hydraulic resistance; improved formation of polyamide (see Table 2)	simultaneously enhanced solute rejection
			CuNPs ⁹⁰		
Nanotubes (1D)			CNTs ^{58, 59, 117, 118}	Gutter effect (analogue to that for gas separation ^{119, 120}) by reducing water transport pathways in polyamide layer; improved interfacial channels with higher aspect ratio of the incorporated nanomaterials; improved formation of polyamide (see Table 2)	
2D materials or interfacial coatings			PDA, ⁶⁷ TA/Fe ³⁺ , ¹²¹ polyphenol/PEI ¹²² , GO ¹²³ and MXene ¹²⁴		
Interfacial voids			Sacrificial nanostrands ⁵⁵		

175 ■ MECHANISTIC INSIGHTS INTO TFNi MEMBRANES

176 Figure 3 shows a comparison of TFNi and TFN membranes. Conventional TFN membranes
177 face a critical limitation of little or limited improvement in water/solute selectivity (also see
178 Figure 2). The random blending of nanomaterials in monomer solutions for TFN (or in
179 substrates for TFCn) can cause severe agglomeration of these nanofillers (see Figure 3a1,2
180 and Ref. ^{18, 19, 53, 71, 125-127}), which not only restricts their loading efficiency⁷¹ but also results
181 in defects formation.⁷³ These challenges can be effectively overcome by incorporating
182 nanofillers as a more ordered interlayer between the substrate and the rejection layer for the
183 case of TFNi. For example, interlayers of AgNPs formed by *in situ* reduction (Figure 3b1)⁵⁷
184 or CNTs prepared by vacuum filtration (Figure 3b2)¹²⁸ present a more uniform loading of
185 nanomaterials, thereby leading to significant enhancement in solute rejection of the resulting
186 TFNi membranes. Furthermore, TFNi membranes often exhibit remarkable improvement in
187 water permeance (sometimes by an order of magnitude, see Figure 2),^{55, 117, 121, 129} which can
188 be attributed to (1) the optimized transport pathways due to the inclusion of a
189 high-permeability interlayer (i.e., the gutter effect^{119, 130-132}) and (2) the improved interfacial
190 polymerization conditions and thus the formation of better-quality polyamide rejection layers
191 (e.g., thinner layers with higher cross-linking degrees^{55, 57, 129}). This section analyzes the
192 detailed mechanisms responsible for enhanced separation performance of TFNi membranes.



193

194 **Figure 3.** Comparison of TFN and TFNi membranes with respect to membrane separation
 195 performance, loading and distribution of nanomaterials, and the corresponding polyamide
 196 structures. Cross-sections of some representative TFN and TFNi membranes are shown in
 197 transmission electron micrographs. The following parts are reprinted with copyright
 198 permission: Part 3a1 from Ref.,¹⁸ Part 3a2 from Ref.¹⁹, Part 3b1 from Ref.,⁵⁷ and Part 3b2
 199 from Ref.¹²⁸

200

201 **Effect of interlayer on transport pathway - the “gutter mechanism”**

202 Despite that numerous experimental studies have demonstrated enhanced water permeance
 203 for TFNi membranes (Figure 2),^{18, 19, 53, 71, 125-127} this phenomenon is somewhat
 204 counterintuitive at the first glance. Based on the resistance-in-series model,^{133, 134} the
 205 inclusion of an additional layer would have increased the overall hydraulic resistance. For
 206 instance, coating a polydopamine layer on a membrane surface decreases its water
 207 permeance.^{98, 135} Nevertheless, the use of polydopamine as an interlayer can lead to an

208 opposite effect of greatly improved water permeance.^{132, 136, 137} These contradictory results
209 can be reconciled by recognizing the effect of a high-permeability interlayer on shortening
210 the transport path through the low-permeability rejection layer (Figure 4a,b). Although this
211 “gutter” effect has been well documented for gas separation membranes^{119, 120, 130, 131}, it has
212 been far less discussed in the context of TFNi membranes used for water filtration.¹³²

213

214 A recent modelling study on the role of substrates by Ramon et al.¹³⁸ can provide some
215 important insights on the transport of water in conventional TFC polyamide membranes.
216 These authors argue that water molecules, after passing through the polyamide rejection layer,
217 have to be collected by the pores in the substrate, i.e., the polymeric matrix of the substrate is
218 assumed to be impermeable. Accordingly, water collected by polyamide far away from a pore
219 region follows a slanted direction through the polyamide layer (Figure 4a), resulting in an
220 effective transport distance that could be an order of magnitude higher than the thickness of
221 the polyamide layer.¹³⁸ Ramon’s model predicts that substrates with a greater number of
222 smaller surface pores are preferred to reduce the transport distance through the polyamide
223 layer and thus increase the water permeance,¹³⁸ which has been experimentally confirmed by
224 Jiang et al.¹³⁹ In this regard, the use of a porous interlayer can effectively meet these criteria
225 and therefore enhance the overall transport efficiency.^{58-60, 132, 140, 141}

226

227 While Ramon’s model¹³⁸ did not explicitly include the effect of the interlayer, the gutter
228 effect has been more systematically investigated through numerical simulations by Kattula et
229 al.¹¹⁹ for gas separation membranes. According to their simulations, the inclusion of a
230 high-permeability gutter layer reduces the effective transport distance through the
231 low-permeability selective layer by making the transport path less slanted (Figure 4b).
232 Intuitively, the gutter effect can be better understood using the concept of the least resistance
233 path, i.e., water transport between any two points assumes a path with the lowest overall
234 hydraulic resistance. Since this overall resistance is contributed by both the transport distance
235 in the selective layer and that in the gutter layer with the latter being more permeable than the

236 former, it is preferred for water to take a shorter transport path in the selective layer (i.e.,
237 closer to the normal direction) at the expense of longer transport path in the gutter layer (i.e.,
238 the incident angle $\theta_1 <$ the refracted angle θ_2 in Figure 4b).

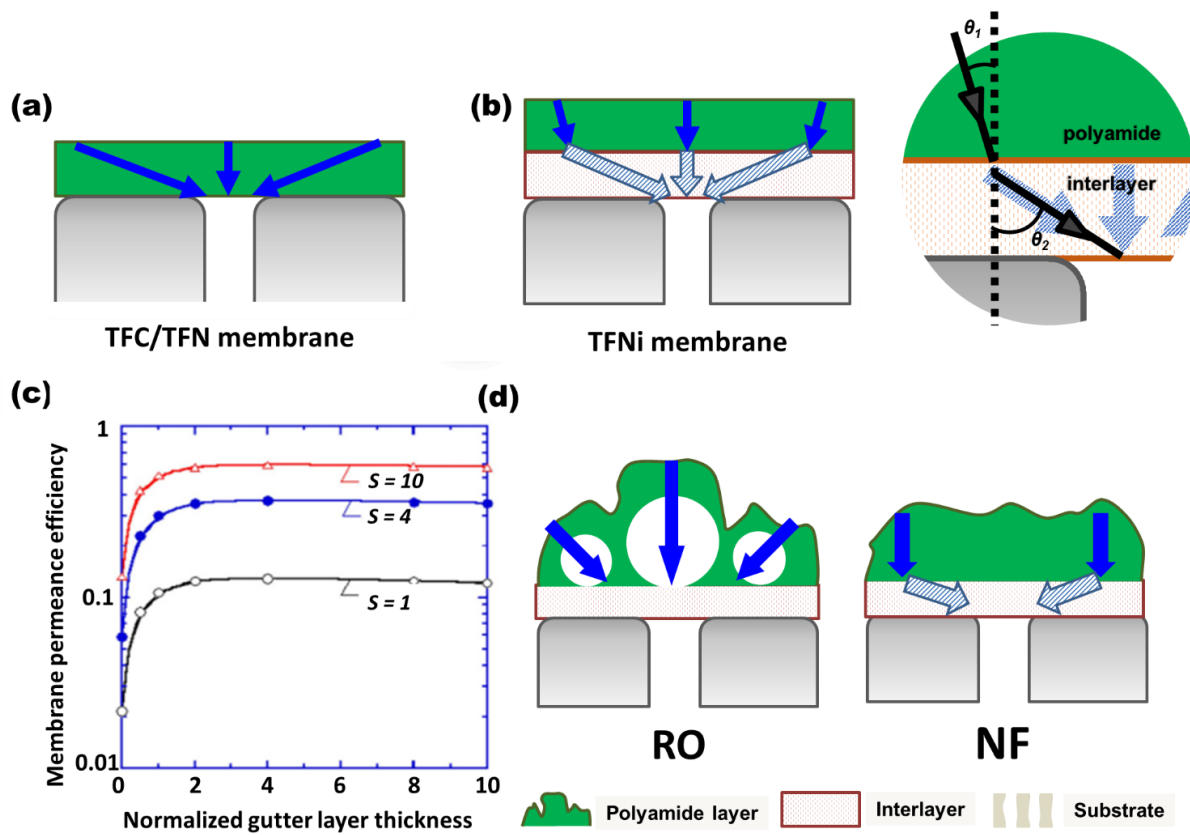
239

240 Although Ramon's ¹³⁸ and Kattula's ¹¹⁹ models provide useful insights, modelling of the
241 gutter effect is not yet available in the context of TFNi RO and NF membranes. In view of the
242 critical role of the gutter effect, quantitative models need to be developed for the optimization
243 of these water filtration membranes, e.g., with respect to the permeability and thickness of the
244 interlayer. Presumably, the permeability of the interlayer must be far greater than that of the
245 polyamide layer to prevent excessive hydraulic resistance through the gutter. The thickness of
246 the interlayer also needs to be optimized to provide effective guttering without suffering
247 severe hydraulic resistance of the gutter layer itself. Future studies should confirm these
248 design principles through both systematic theoretical modelling and experimental validation.
249 Furthermore, the role of the interlayer on solute transport and thus on water-solute selectivity
250 needs to be investigated systematically.

251

252 A detailed survey of literature data (Figure 2a) further reveals that the TFNi strategy tends to
253 be more effective in enhancing water permeance for interlayered NF membranes formed by
254 PIP and TMC (up to an order of magnitude enhancement ^{121, 129, 142, 143}) compared to
255 interlayered RO membranes formed by MPD and TMC (1 - 3 fold enhancement^{57, 68, 144}). This
256 observation is contradictory to Ramon's ¹³⁸ and Kattula's ¹¹⁹ models (Figure 4c) that would
257 predict the greater influence of interlayers (or substrate properties) for membranes with
258 thinner rejection layers, noting that the intrinsic polyamide film thicknesses for RO
259 membranes (approximately 10 - 20 nm^{142, 143}) are usually smaller than those of NF
260 membranes (typically on the order of 100 nm^{121, 129}). This disparate observation can be
261 potentially explained by the nanovoid-containing structure of polyamide films formed via the
262 interfacial polymerization of MPD and TMC - the state-of-the-art chemistry for polyamide
263 RO membranes (Figure 4d and Refs.^{91, 142, 143, 145, 146}). Originated from interfacial degassing

264 (e.g., the release of CO_2 gas bubbles from the HCO_3^- -rich MPD solution under the combined
 265 effects of interfacial heating and H^+ generation during interfacial polymerization^{91, 92, 147-149}),
 266 these nanovoids with negligible hydraulic resistance would provide a self-guttered effect,
 267 rendering any additional gutter layers less effective in further enhancing the water permeance.
 268 In contrast, polyamide layers formed by the PIP/TMC chemistry typically contain fewer or no
 269 interior voids, resulting in a more marked gutter effect with the TFNi approach. Future
 270 studies should systematically investigate the detailed mechanisms involved in both
 271 MPD/TMC and PIP/TMC chemistries for the optimization of separation performance of
 272 TFNi membranes.
 273



274

275 **Figure 4.** The gutter effect in TFNi membranes. (a) Schematic illustration of water transport
 276 path in a TFC/TFN membrane. The average transport path through the polyamide layer is
 277 significantly longer than the thickness of the polyamide layer. (b) Schematic illustration of
 278 water transport path in a TFNi membrane. To minimize the overall hydraulic resistance, water
 279 will take a shorter path in the less permeable polyamide layer at the expense of a longer path
 280 in the more permeable interlayer, causing the incident θ_1 to be greater than the refracted angle
 281 θ_2 . (c) Simulation of the gutter effect for gas separation membranes. The horizontal axis

282 shows the normalized gutter layer thickness, i.e., the ratio of gutter layer thickness over the
283 substrate pore radius. The vertical axis shows the membrane permeance efficiency, i.e., the
284 permeance of the composite membrane over the ideal permeance of the selective layer (with
285 the latter obtained assuming all the transport paths are normal to the selective layer). The
286 simulation is performed for three different scaled selective layer thickness ($S = 1, 4$ and 10),
287 where S is the ratio of selective layer thickness over the substrate pore radius. Other
288 simulation conditions include: substrate porosity = 1% and the gutter layer is 10 times as
289 permeable as the selective layer. (d) Schematic illustration of the gutter effect in RO and NF
290 TFNi membranes, respectively. Figure 4c was modified from reference¹¹⁹ with copyright
291 permission.

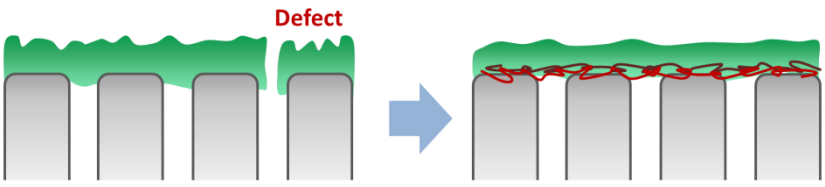
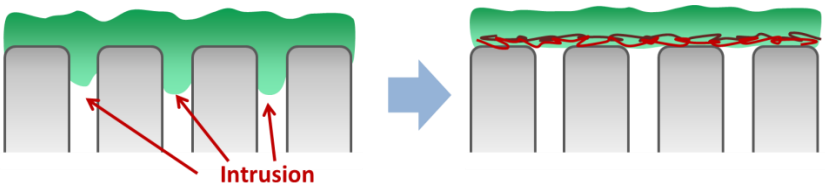
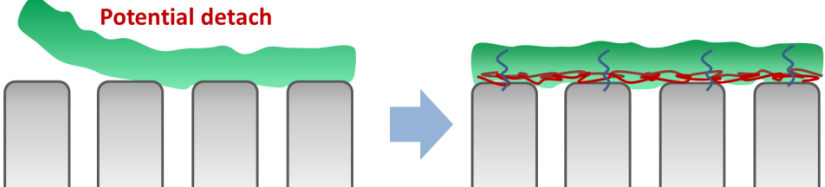
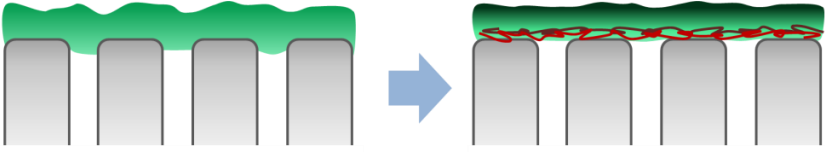
292

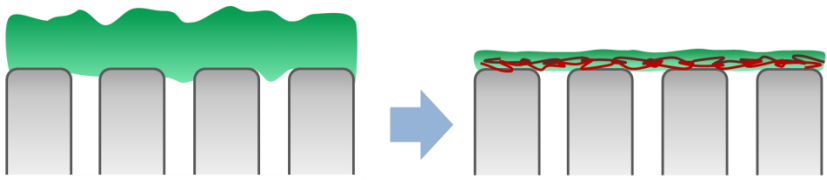
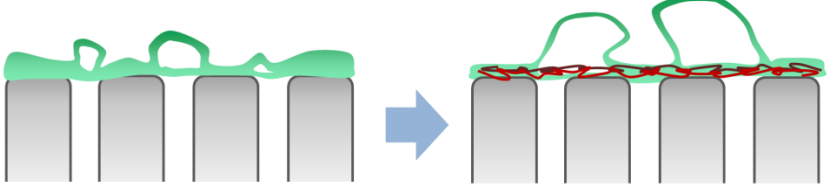
293 **Effect of interlayer on the formation of polyamide rejection layer**

294 In addition to the important gutter effect, the interlayer can also significantly change the
295 formation of the polyamide rejection layer due to its influence on the interfacial
296 polymerization reaction via (1) changing the reaction interface,^{55, 121} (2) affecting the uptake
297 and release of the amine monomers,^{55, 121} and/or (3) enhancing the confinement effect to
298 interfacially degassed nanobubbles.¹⁵⁰ These effects and their impact on the physicochemical
299 properties on the TFNi membranes, summarized in Table 2, are discussed in detail in this
300 section.

301

302 **Table 2.** The effect of interlayer on the formation of polyamide rejection layer.

Role of interlayer	Schematic illustration		Effect on membrane morphology/chemistry	Effect on separation performance
	TFC	TFNi		
Improved reaction interface				
Improved uniformity, reduced surface pore size, reduced surface roughness, and/or enhanced surface hydrophilicity			Minimizing defects in polyamide rejection layers ^{121, 122}	Improved selectivity ^{151, 152}
Reduced surface pore size			Eliminating intrusion of polyamide into substrate pores ^{117, 121, 132}	Enhanced water permeance by preventing the “bottleneck” effect ^{117, 121, 132}
Improved interfacial stability			Reactive/functional interlayers firmly bound to the polyamide rejection layer with improved stability ^{67, 69}	Improved selectivity ^{67, 122, 136}
Enhanced sorption of amine monomers				
Increased effective amine monomer concentration			Enhanced polyamide crosslinking degree ¹³²	Improved selectivity ^{57, 153}
Controlled release of amine monomers				

<p>Reduced release rate of amine monomers and slowing down their diffusion</p>		<p>Thinner and smoother polyamide rejection layer^{55, 129}</p>	<p>Improved water permeance^{55, 129}</p>
<p><i>Enhanced confinement effect for interfacially-degassed nanobubbles</i></p>			
<p>Better confinement of interfacially degassed nanobubbles</p>		<p>Rougher polyamide surfaces with more extensive nanovoids^{66, 132, 150}; possibly reduced intrinsic polyamide thickness^{142, 146, 147, 149, 154}</p>	<p>Increased filtration area; hence improved membrane permeance^{66, 132, 150}</p>

304 **Improved reaction interface.** The inclusion of an interlayer can significantly change the
305 properties of the reaction interface, e.g., improved uniformity, reduced surface pore size,
306 reduced surface roughness, and/or enhanced surface hydrophilicity.^{59, 124, 150, 151} These
307 improved surface properties are beneficial to minimize the formation of defects in the
308 polyamide rejection layer and thus improve the selectivity of the resulting TFNi membranes
309 (Table 2).^{117, 121, 151} In addition, the shift of the reaction interface and the smaller surface pore
310 size can prevent the intrusion of polyamide into the substrate pores (Table 2).^{117, 121} In
311 contrast, the intrusion of polyamide into substrate pores have been reported for conventional
312 TFC membranes (particularly when relatively large substrate pores are used),^{117, 118, 121, 149, 155}
313 which can present a “bottleneck” effect to significantly reduce their water permeance.¹²¹

314

315 In some cases, the functional groups introduced to the interlayer can also participate in the
316 interfacial polymerization reaction [e.g., the reaction between -OH groups of PDA and
317 polyvinyl alcohol (PVA) with TMC to form ester bonds], which tends to improve membrane
318 rejection.^{151, 152} In view of the poor interfacial stability of conventional TFC membranes (due
319 to the lack of chemical bonding between the polyamide layer and the substrate and their
320 different swelling tendency⁶⁷), the use of a reactive/functional interlayer can be effective in
321 address this problem. For example, several studies have reported the effective use of
322 polydopamine^{67, 69, 132, 136, 156} and PVA^{151, 152, 157} to effectively enhance the interfacial strength.
323 Reactive/functional interlayers can firmly attach the polyamide rejection layer to the substrate
324 through covalent bonding,^{158, 159} hydrogen bonding^{69, 160}, and/or electrostatic attraction,^{68, 161}
325 thereby enhancing the membrane performance stability in terms of water flux and salt
326 rejection.^{67, 162} Future studies should further explore the tailoring of physical binding and
327 chemical bonding of the interlayer to the polyamide layer and to the substrate.

328

329 **Enhanced sorption of amine monomers.** Recent studies show that some interlayer materials
330 (e.g., polyphenol^{121, 122}, polydopamine⁶⁹ and polyvinyl alcohol^{151, 152}) can significantly
331 increase the sorption of amine monomers, sometimes by orders of magnitude.¹²¹ The

332 enhanced uptake of MPD or PIP monomers can be attributed to the enhanced hydrophilic
333 interaction^{57, 163} or chemical bonding.^{67, 121} According to the existing literature on interfacial
334 polymerization, increasing the effective amine monomer concentration is beneficial to form a
335 more highly crosslinked rejection layer.^{68, 149, 164, 165} In addition, the enhanced amine uptake
336 may further minimize the formation of defects in the rejection layer.⁵⁵ Indeed, many studies
337 on TFNi (e.g., using interlayers of AgNPs⁵⁷, CNTs⁵⁹, GO¹⁶⁶ and coating layers of
338 polydopamine^{132, 156} and tannic acid/Fe³⁺¹²¹) reported enhanced rejection of various solutes
339 (e.g., NaCl^{68, 71}, Na₂SO₄^{118, 121}, neutral solutes^{57, 136} and some trace organic compounds^{57, 132}).

340

341 ***Controlled release of amine monomers.*** The presence of an interlayer can significantly
342 reduce the release rate of amine monomers and slow down their diffusion, which tends to
343 create thinner polyamide layers with smoother surface (Table 2).^{55, 68, 121, 129} For instance, a
344 desorption study using a quartz crystal microbalance with dissipation (QCM-D) show that a
345 tannic acid (TA)/Fe³⁺ interlayer slowed down the release rate of PIP by nearly an order of
346 magnitude compared to the bare polysulfone substrate.¹²¹ This controlled release of amine
347 monomers results in a more uniform and thinner polyamide rejection layer. The thinner
348 rejection layer together with other beneficial effects for the resulting TFNi (e.g., the gutter
349 effect and the elimination of polyamide intrusion) led to an order of magnitude improvement
350 in water permeance compared to the control TFC NF membrane.¹²¹ Likewise, Lee et al.⁶⁸
351 observed a significantly smoother and thinner polyamide rejection layer of a TFNi RO
352 membrane using a polyelectrolytes-based interlayer. These authors further demonstrated
353 reduced organic fouling of the TFNi membrane, possibly attributed to its much smoother
354 membrane surface.

355

356 ***Enhanced confinement effect for interfacially-degassed nanobubbles.*** Although some
357 studies reported reduced surface roughness for TFNi membranes,^{55, 68} other researchers
358 observed the opposite trend of increased surface roughness.^{121, 150} The latter can be explained
359 by the gas confinement effect during an interfacial polymerization reaction. According to the

360 nano-foaming theory, the byproducts (H^+ and heat) of interfacial polymerization reaction
361 converts bicarbonate in the high-pH amine solution into CO_2 gas bubbles, i.e., $HCO_3^- + H^+$
362 $\xrightarrow{\Delta} CO_2\uparrow + H_2O$.^{91, 92, 148} These nanosized gas bubbles, if sufficiently retained by the substrate
363 and subsequently encapsulated by the polyamide film, are responsible for the nanovoids
364 contained in rejection layers (particularly those formed by the MPD/TMC chemistry) and
365 their ridge-and-valley surface roughness.^{147, 149} The inclusion of an interlayer can
366 significantly decrease the surface pore size, resulting in better confinement of the
367 nanobubbles (i.e., preventing the gas bubbles from escaping through the porous substrate
368 during the interfacial polymerization reaction) and therefore rougher polyamide surfaces.¹⁵⁰
369 According to the literature, the greater surface roughness created by better confinement
370 effects can significantly increase the effective filtration area and also possibly decrease the
371 intrinsic thickness of the polyamide film, therefore leading to improved water permeance.^{142,}
372 ^{146, 147, 149, 154}

373

374 The above mechanisms may compete with each other in some cases. For example, while the
375 slower release of monomers tends to favor a smoother membrane surface,^{55, 68} the greater
376 amine monomer uptake and enhanced confinement effect tend to promote a greater surface
377 roughness through improved nano-foaming conditions.^{132, 149, 150} The resultant membrane
378 morphology is, therefore, an interplay of the various effects, with the nano-foaming effects
379 more dominating for the MPD/TMC chemistry and the smoothing effect more dominating for
380 the PIP/TMC chemistry. Likewise, the better amine uptake can increase the crosslinking of
381 the polyamide,^{57, 69, 153} yet its slower release may cause an opposite effect.^{121, 163, 167} These
382 competing effects need to be systematically investigated in future studies.

383

384 ■ MATERIALS AND PREPARATION METHODS FOR TFNi MEMBRANES

385 Materials used for interlayers can be classified into nanoparticles, 1D nanotubes or nanowires,
386 2D nanosheets or nanoplates, as well as interfacial coatings (Table 1 and Figure 5). In
387 addition, the nanofillers used for interlayers can be porous or nonporous. Examples of
388 nanoparticles used in TFNi membranes include AgNPs,⁵⁷ TiO₂,^{56, 115} carbon quantum dots
389 (CQDs)^{168, 169} and FeO¹⁷⁰. These solid hydrophilic nanoparticles can induce the formation of
390 interfacial channels around the nanoparticles (Figure 5a).^{57, 81} For example, Yang et al.⁵⁷
391 observed selective nanochannels of approximately 2.5 nm in size, which are attributed to the
392 hydrolysis of TMC monomers by water molecules adsorbed on the nanoparticles during the
393 interfacial polymerization reaction. These interfacial channels led to a tripled water
394 permeance together with the enhanced rejection of NaCl, boron, and a range of organic
395 molecules. In contrast, the use of solid hydrophobic nanoparticles (e.g., CuNPs) may cause a
396 reduction in permeance due to the lack of such interfacial channels. Porous nanoparticles are
397 also frequently reported for TFNi membranes, such as zeolite,¹¹⁶ MOFs (ZIF-8,^{63, 64, 171-173}
398 ZIF-67,⁶³ ZIF-93,¹⁷⁴ UiO-66^{65, 175} and HKUST-1¹⁷⁴), and covalent organic framework
399 (COF)¹²⁹, whose interior channels may further enhance water permeance.⁸¹

400

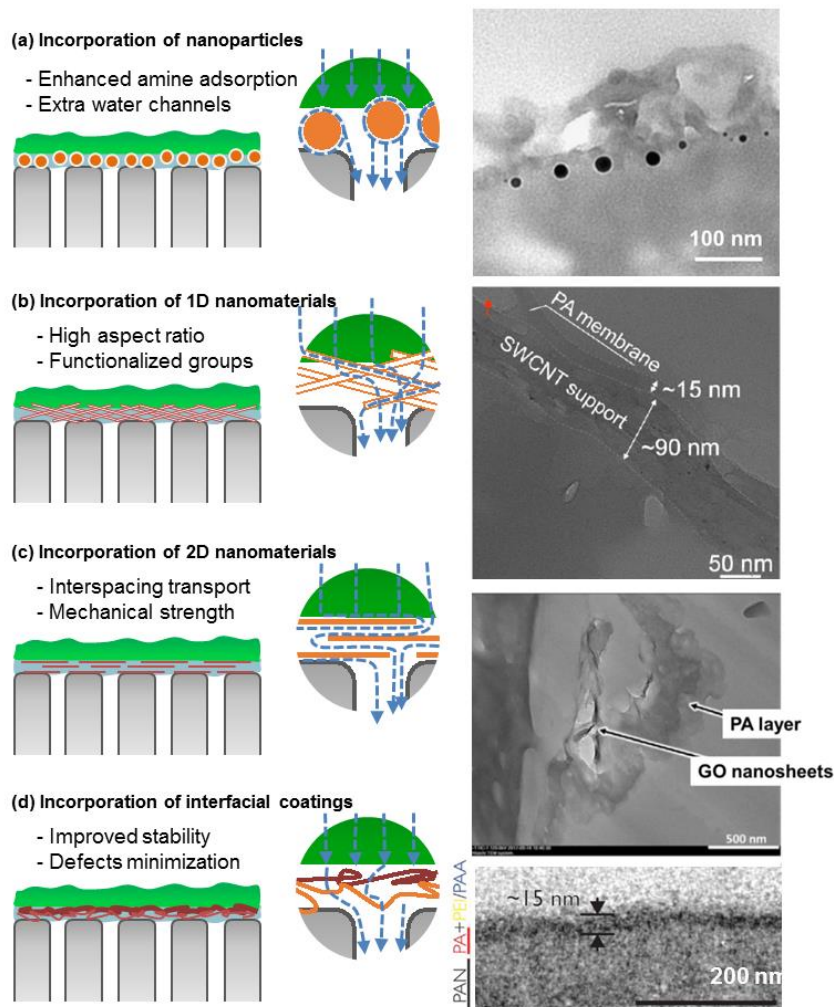
401 Nanofillers with higher aspect ratios have also been widely reported for TFNi membranes.
402 Examples including 1D nanomaterials (Figure 5b) such as carbon nanotubes (CNTs)^{58-60, 140,}
403 ¹⁴¹ and their derivatives,^{58, 118, 128, 144, 176} Cd(OH)₂ nanostrands/nanowires,⁵⁵ cellulose
404 nanocrystals,¹⁶³ and halloysite nanotube¹⁷⁷ and 2D nanomaterials (Figure 5c) such as
405 graphene oxide (GO)^{123, 159, 178} and their derivatives^{61, 141} and MXene¹²⁴. In addition, highly
406 permeable interfacial coatings (Figure 5d) have been used, such as polydopamine^{67, 136, 137, 156,}
407 ¹⁷⁹ and its derivatives,^{69, 71} polyethyleneimine (PEI) and its derivatives^{68, 69} polyphenols,¹²²
408 tannic acid/Fe³⁺ nanoscaffold,¹²¹ porous organic polymer,¹⁸⁰ PDA/COFs,¹⁵³
409 MOFs/Noria/PEI⁷⁰ and gelatin¹⁶⁷. Figure 6 compares the enhancement of water permeance
410 and water/salt selectivity for different types of materials. On average, NPs double the water
411 permeance but with relatively insignificant enhancement in selectivity. Interestingly, 1D

412 nanofillers are more effective in enhancing water permeance, which is probably associated
413 with the greater interfacial area as a result of their high length-to-width aspect ratio.
414 Compared to 1D materials, interlayers formed by 2D nanomaterials (e.g., lamellar layers of
415 GO⁶² or MXene¹²⁴ prepared with vacuum filtration) are on average less effective in
416 enhancing water permeance but more effective in improving selectivity, which is likely due to
417 the relatively tortuous transport path in such lamellar structures (Figure 5c).^{181, 182} A possible
418 further improvement is the use of porous 2D nanosheets (e.g., MoS₂¹⁸³ and 2D MOFs^{66, 184})
419 as interlayer materials, whose defined nanopores may facilitate the fast transport of water
420 molecules while selectively retaining the target solutes. Future studies need to systematically
421 investigate the detailed roles of materials geometry (e.g., size, shape, and aspect ratio) and
422 porosity (e.g., porous 2D nanosheets) on the separation performance of TFNi membranes.

423

424 Among all the materials, interfacial coatings appear to be the most effective to achieve
425 enhanced membrane separation (Figure 6). This trend may be explained by the
426 ultrapermeable and continuous nature of these interlayer coatings, which results in more
427 efficient gutter effect (Figure 4) compared to discrete NPs, 1D, or 2D nanomaterials. In
428 addition, some interfacial coating materials are more effective in minimizing defects in the
429 rejection layer and their specific chemistry may improve membrane integrity.⁶⁷ A good
430 example is polydopamine, whose catechol, amine and hydroxyl groups can form covalent
431 bonds with diamine monomers through Michael addition and/or Schiff base reaction.^{67, 185}

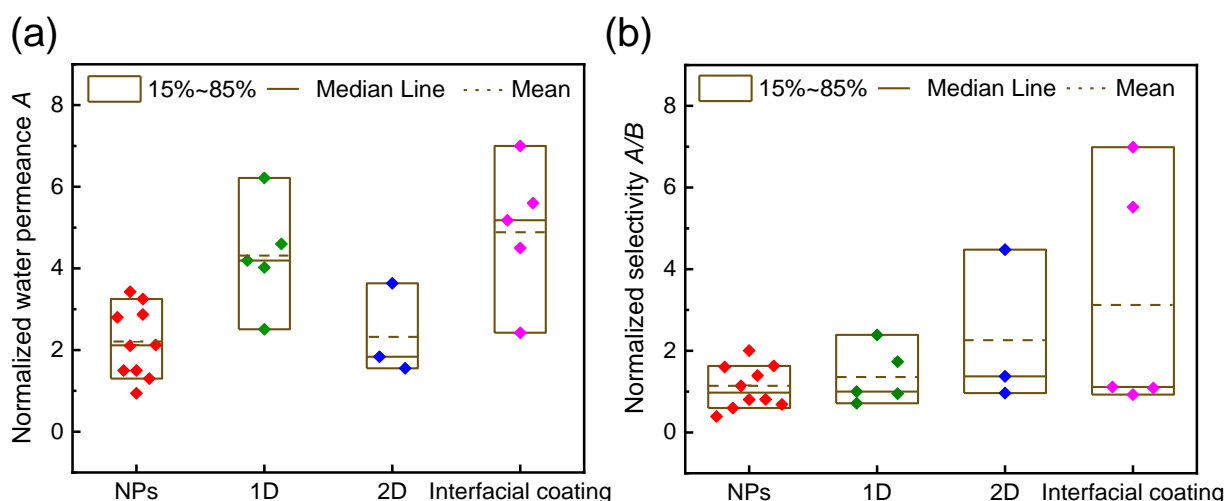
432



433

434 **Figure 5.** Schematic illustrations (left panel) and transmission electron micrographs (right
 435 panel) of TFNi membranes incorporated with (a) NPs, (b) 1D, (c) 2D nanomaterials and (d)
 436 interfacial coatings as interlayers. The TEM images are reprinted from references (NPs,⁵⁷
 437 1D,⁵⁹ 2D¹⁷⁸ and interfacial coating-based⁶⁸) with copyright permissions.

438



439

440 **Figure 6.** Statistical analysis of (a) normalized water permeance A and (b) normalized
 441 selectivity A/B for TFNi membranes based on NPs,^{64, 65, 71, 115, 129, 171, 173, 186} 1D,^{55, 58, 117, 118, 140},
 442 2D materials,^{62, 123, 124} and interfacial coating^{70, 121, 122, 132, 187}. The water permeance A and
 443 selectivity A/B have been normalized by their respective control TFC without the interlayer.
 444 The A/B values were based on simple salts (NaCl for RO membranes and Na₂SO₄ for NF
 445 membranes).

446

447 The general fabrication routine for TFNi membranes is to first form a uniform layer of
 448 nanomaterials or interfacial coating prior to the interfacial polymerization reaction. A wide
 449 range of available methods have been explored in the literature, such as *in situ* growth,⁷¹
 450 evaporation,⁶⁵ vacuum filtration,¹²⁹ covalent bonding,⁶⁹ co-deposition,⁷⁰ dip coating,⁶⁷ spray
 451 coating,¹⁷³ spin coating,¹⁶⁶ electrospraying coating¹⁸⁸ and brush coating⁵⁹ (see details in
 452 Supporting Information S1). It is important to note that some fabrication methods may not be
 453 cost-effective and could be difficult to scale up. For instance, the spin coating method¹⁶⁶ may
 454 face the challenge of material loss and difficulties in mass production. Similarly, vacuum
 455 filtration may face the constraints of small membrane area and the stability of the filtered
 456 layer of nanomaterials. Interlayers based on nanoparticles or nanotubes, e.g., formed by *in*
 457 *situ* growth or vacuum filtration, may be subject to concerns of loss/leaching of nanomaterials
 458 in addition to the high fabrication cost. In this regard, coating layers formed by conventional
 459 dip coating can be more cost competitive and more readily integrated with existing
 460 membrane production lines, considering the fact that PVA surface coating has already been

461 routinely applied in the post-treatment of commercial RO membranes.¹⁸⁹⁻¹⁹¹ Coating layers
462 prepared by spraying (including electrospraying) could also be potentially scaled up, although
463 their commercial viability needs to be further assessed (e.g., through pilot scale production
464 lines).

465

466 ■ ENVIRONMENTAL APPLICATIONS

467 The high water permeance and better selectivity of TFNi membranes may enable them to be
468 used for a wide range of applications to potentially achieve reduced energy consumption
469 and/or improved product water quality (Table 3). This section summarizes some important
470 applications scenarios and then analyzes the potential benefits and limitations of TFNi
471 membranes for these applications.

472

473 **Application Scenarios**

474 *Seawater and brackish water desalination.* RO-based seawater (SWRO) desalination has
475 been increasingly used in many coastal regions facing a shortage of freshwater supply.^{2, 5, 192}
476 A typical seawater has a total dissolved solids (TDS) content in the range of 32-35 g/L, which
477 means that salt removal is the primary treatment objective. The high TDS and thus the
478 elevated osmotic pressure (on the order of 25 bar) dictates a high specific energy
479 consumption (SEC) of approximately 2 kWh/m³ for the first pass SWRO.¹⁹³⁻¹⁹⁶ Boron is
480 another important contaminant to be removed during SWRO,¹⁹⁷⁻²⁰⁰ with the World Health
481 Organization and European Union guideline boron concentrations for drinking water of 2.4
482 mg/L²⁰¹ and 1.0 mg/L,²⁰² respectively. Due to its small molecular size and neutral charge at
483 typical environmental pHs (pKa of boron = 9.25), commercial SWRO membranes generally
484 have low to moderate boron rejection of 40-80%.^{199, 203, 204} For this reason, many SWRO
485 plants implement a two-pass RO treatment, where the second-pass RO together with pH
486 adjustment is designed to ensure sufficient boron removal. This requirement of an additional
487 second-pass RO can significantly increase the overall cost, SEC and footprint of seawater
488 desalination. In addition to boron, the presence of bromide in desalinated water can be a
489 concern in some cases due to the potential formation of bromide-containing
490 disinfection-byproducts (DBPs) upon chlorination.^{100, 205-209} Some plants in Israel also
491 implement a second-pass RO to meet the stringent chloride requirement to prevent corrosion
492 of pumps/pipelines.²¹⁰ Similar to SWRO, RO-based brackish water (BWRO) desalination

493 aims primarily for TDS removal. Compared to SWRO, BWRO has much lower SEC thanks
494 to its lower TDS and osmotic pressure.

495

496 **Water reuse.** Membrane-based water reuse of municipal wastewater was first practiced at the
497 Water Factory 21 in Southern California and has been gaining increasing popularity in recent
498 decades due to its relatively low SEC compared to seawater desalination.⁷ Since the TDS
499 content of typical municipal wastewater is much lower than that of seawater, the removal of
500 TDS is generally a less critical challenge in the context of membrane-based water reuse.^{98,211}
501 In contrast, trace organic contaminants (TrOCs), such as DBPs, pharmaceutically active
502 compounds (PhACs), endocrine-disrupting compounds (EDCs), herbicides, pesticides, and
503 antibiotics, are of greater concern due to their potential effects on human health.^{7, 98, 212, 213}
504 Commercial TFC membranes, though well optimized for the rejection of TDS, often show
505 insufficient removal of some toxic TrOCs such as the small molecular-weight DBP
506 N-nitrosodimethylamine (NDMA) and many hydrophobic EDCs.⁷ In addition, membrane
507 integrity and the removal of viruses are critical issues for potable water reuse.^{7, 142, 214, 215}

508

509 **Drinking water treatment.** NF membranes can be applied for groundwater treatment for the
510 partial removal of hardness and TDS. Both RO and NF membranes have also been applied to
511 treat arsenic-contaminated groundwater.^{216, 217} Increasing number of publications have also
512 investigated the use of RO and NF membranes for the removal of TrOCs, such as
513 polyfluorinated alkyl substances (PFASs), PhACs, DBPs, EDCs, antibiotics in surface and/or
514 ground water.^{98, 99, 212, 218-220}

515

516 **Industrial wastewater treatment and reuse.** RO and NF membranes have been applied in a
517 variety of industrial wastewater treatment and/or reuse applications to target the removal of
518 hardness, dissolved organic matter, heavy metals, sulphate, nutrients, and other
519 industrial-specific hazardous chemicals.²²¹⁻²²⁴ Membrane selectivity plays a critical role in

520 these applications to ensure high treatment efficiency and reliability.

521

522 **Resource recovery.** Resource recovery presents additional opportunities for
 523 high-performance RO and NF membranes. Notable examples include the recovery of
 524 high-value metals (e.g., lithium or palladium),^{225, 226} dyes molecules,²²⁷⁻²³¹ and nutrients (e.g.,
 525 nitrogen and phosphorous)^{232, 233}. Some of these applications may require high solute/solute
 526 selectivity (e.g., $\text{Li}^+/\text{Mg}^{2+}$ for the case of lithium extraction from brine²²⁵) in addition to high
 527 water permeance and high water/solute selectivity.^{225, 234}

528

529 Table 3. Potential environmental applications of TFNi membranes.

Applications	Target contaminants	Remarks	Refs
Seawater desalination	TDS	High TDS of 32-35 g/L for seawater; high osmotic pressure	2, 235, 236
	Boron	Low boron removal (typically 40-80%) by commercial RO membranes. WHO guideline concentration of 2.4 mg/L for drinking water. Many SWRO plants install a second RO treatment for boron removal.	197, 200, 203, 237
	Bromide	Potential formation of toxic DBPs upon chlorination	209, 238-241
	Chloride	Potential corrosion issues. Resulted in a second-pass RO in some SWRO plants in Israel.	210
Water reuse	TDS	Partial removal of TDS	7, 242, 243
	NDMA	A notorious DBP and a suspected carcinogen. Low rejection by RO membranes (20 – 80%). Notification level of 10 ng/L in California.	7, 244-246
	Other TrOCs, such as DBPs, PhACs, EDCs, and antibiotics	Many of TrOCs are toxic. Some are poorly removed by RO membranes (e.g., hydrophobic EDCs and some neutral hydrophilic compounds with small molecular weights).	97, 98, 174, 212, 247
	Viruses	Incomplete removal of viruses due to the presence of defects in membranes and modules.	214, 248-250
Drinking water treatment	Hardness (Ca^{2+} and Mg^{2+})	Commercial NF membranes are often negatively charged, which reduce the removal efficiency for Ca^{2+} and Mg^{2+}	251-253
	Arsenic, selenium, uranium	Toxic metals in some ground water. Low removal for neutrally charged As(III) by RO/NF membranes.	216, 217, 254, 255

	Perfluorochemicals (PFCs)	Toxic compounds with extremely high persistence. Examples include perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS).	218, 219, 256-258
	Other heavy metals and TrOCs	Toxic chemicals	98, 99, 212, 219, 220, 259
Industrial wastewater treatment	Hardness, sulphate, silica, colloids, and dissolved organic carbon in cooling tower blowdown water and paper mills	Prone to fouling and scaling. Requirement for specific solute/solute selectivity.	221, 260, 261
	Heavy metal ions (Cr, Ni, etc.) in mining, electroplating, etc.	Requirement for the removal of industry-specific heavy metals	222, 262-266
Resource recovery	Precious metal recoveries, such as lithium (Li) or palladium (Pd)	Often suffering from low ion-ion selectivity	225, 226, 234, 267
	Nutrients, such as nitrogen (N) and phosphorous (P)	Low removal of N in some cases	232, 233, 268
	Dyes recovery in textile wastewater	Requirement for dye/salt selectivity in addition to dye/water selective and high water permeance	227-230, 269, 270

530

531 **Assessment of the Potential of TFNi membranes for reduced energy consumption**

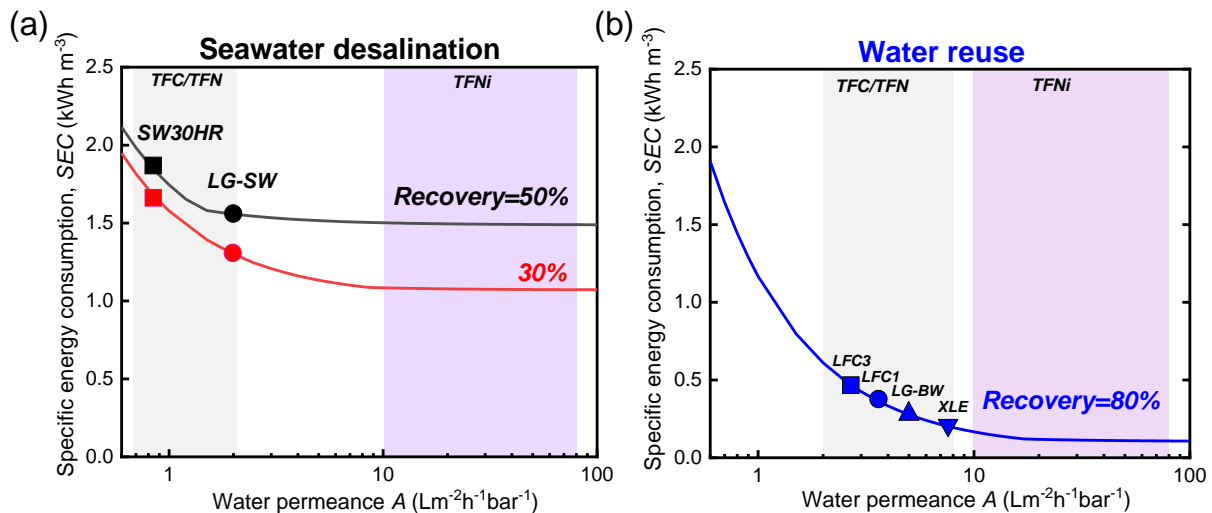
532 A frequently claimed benefit of “ultrapermearable” membranes in the existing literature is the
533 potential for reducing the SEC. Since TFNi membranes could provide up to an order of
534 magnitude improvement in water permeance, it is interesting to evaluate their potential
535 energy saving in different applications. Figure 7a presents the typical scenario of SWRO
536 desalination (osmotic pressure of 25 bar for seawater, ~ 50% water recovery ratio (WRR) for
537 large scale SWRO plants or 30% for some smaller plants). Commercially available TFC and
538 TFN SWRO membranes are used for benchmarking purpose. Despite the ultra-high water
539 permeance of TFNi membranes (e.g., > 10 Lm⁻²h⁻¹bar⁻¹), limited savings in SEC can be
540 achieved at a WRR of 50% (e.g., approximately 16.6% reduction in SEC for a TFNi
541 membrane of 15 Lm⁻²h⁻¹bar⁻¹ ²⁷¹ vs. a TFC membrane of 1 Lm⁻²h⁻¹bar⁻¹). This marginal
542 reduction in SEC is largely due to the dominance of energy consumption by the high osmotic
543 pressure of seawater.^{193, 194, 272} Similarly, Cohen-Tanugi et al.¹⁹⁵ suggested that a tripled water
544 permeance would only result in approximately 15% saving in SEC in the context of SWRO

545 desalination. Interestingly, at a lower WRR of 30% (applicable for some smaller-scale SWRO
546 desalination plants), a much more attractive energy saving is feasible (e.g., 46.1% reduction
547 in SEC for the same TFNi membrane), thanks to the lower osmotic pressure of the
548 desalination brine (35.7 bar at 30% WRR vs. 50 bar at 50% WRR).

549

550 The potential for energy saving is much more significant for applications involving
551 low-osmotic-pressure feed waters, for which the hydraulic resistance of the membrane plays
552 a dominant role in dictating the applied pressure and thus the SEC related to a given
553 membrane process. Here we consider a typical water reuse application with a feed water
554 osmotic pressure of ~ 0.5 bar and a WRR of 80% (Figure 7b). Compared to the commercial
555 BWRO membranes, the use of TFNi membranes can achieve > 80% reduction in SEC (e.g.,
556 compared to the commercial LFC3 membrane). A similar reduction of SEC is expected for
557 other applications involving low-osmotic-pressure feed waters. Some studies suggested the
558 use of ultra-permeable membranes for saving the footprint of membrane plants, i.e., by
559 applying the same or similar applied pressure (without energy savings) but using less
560 membrane area.¹⁹⁵ This strategy can potentially lead to significant savings in capital cost (e.g.,
561 reduced membrane area, fewer pressure vessels, and reduced building size). Nevertheless, the
562 approach inevitably demands the application of higher water fluxes, which could promote
563 more severe concentration polarization and fouling.²⁷³ Therefore, future studies need to
564 systematically investigate the fouling issues for TFNi membranes.

565



566

567 Figure 7. The relationship between specific energy consumption (SEC, KWh m⁻³) and
 568 membrane water permeance (Lm⁻²h⁻¹bar⁻¹) in the context of (a) seawater desalination and (b)
 569 water reuse. Commercial membranes used for benchmarking include a TFC membrane
 570 SW30HR and a TFN membrane LG-SW for seawater desalination; and TFC membranes
 571 LFC3, LFC1, and XLE and a TFN membrane LG-BW for water reuse).^{48, 49, 274} Water
 572 permeance results of TFNi membranes were adopted based on Figure 2. For SEC calculations
 573 of seawater desalination, the osmotic pressure is set at 25 bar (TDS of approximately 32000
 574 ppm). Two water recovery ratios (WRR) are evaluated, with WRR = 50% applicable for
 575 large-size SWRO plant and 30% for some smaller plants. For water reuse applications, the
 576 osmotic pressure is set at 0.5 bar (TDS of approximately 600 ppm) with a WRR of 80%. The
 577 detailed calculation of energy consumptions can be found in Supporting Information S2.

578

579 Assessment of the Potential of TFNi membranes for improved treatment efficiency

580 The selectivity of a membrane plays a critical role in its treatment efficiency, e.g., the
 581 rejection of contaminants in desalination, wastewater treatment, and water reuse or the
 582 recovery ratio in resource recovery applications.^{6, 7, 193, 225, 259, 275, 276} Existing literature on
 583 TFNi membranes have been heavily focusing on the removal and selectivity respect to
 584 common inorganic salts and ions, such as NaCl,^{57, 68} Na₂SO₄ (or SO₄²⁻),^{121, 151} Ca²⁺,^{187, 277} and
 585 Mg²⁺.^{71, 122} Compared to their TFC controls, TFNi membranes generally show improved
 586 selectivity for these contaminants (Figure 2b and Figure 6b). The enhanced selectivity can be
 587 attributed to (1) the increased crosslinking degree^{57, 69, 153} and fewer defect regions^{57, 121, 122} in
 588 the polyamide layer and (2) the creation of selective transport channels including interior
 589 channels of the nanomaterials/coatings^{97, 98} or the interfacial channels formed between the

590 nanofillers and polyamide^{57, 81}). However, it is worthwhile to note that conventional TFC
591 membrane has already been highly optimized for salt removal.^{98, 247} For example, fully
592 aromatic RO membranes based on the MPD/TMC chemistry can easily achieve high NaCl
593 rejections of > 99%.^{6, 190, 191} Likewise, semi-aromatic NF membranes based on the PIP/TMC
594 chemistry show high rejection against divalent ions (e.g., >99% for Na₂SO₄).^{37, 274, 278} In
595 contrast, these membranes often show insufficient rejections of some important contaminants
596 such as boron,^{197, 200, 203, 237} heavy metals,^{216, 217, 255} and TrOCs.^{97, 98, 174, 212, 247} In this regard, it will
597 be highly valuable to investigate the effectiveness of TFNi for these important solutes.

598

599 Despite the critical importance of adequate removal of TrOCs for potable water reuse
600 applications^{7, 259, 279, 280} and boron for desalination applications^{197, 200, 203, 237}, only handful
601 studies have investigated the applicability of TFNi membranes for this purpose.¹³² In
602 principle, improved physicochemical properties of TFNi membranes (e.g., higher
603 crosslinking degree^{57, 69, 153}, less defect regions^{121, 122}, enhanced charge interaction,^{71, 158} etc.)
604 and the presence of selective interior/interfacial channels would contribute to better removal
605 of these contaminants. For example, Yang et al.⁵⁷ demonstrated the use of hydrophilic AgNPs
606 for the creation of selective interfacial channels for the effective enhancement of water
607 permeance. The resulting TFNi membrane showed increased selectivity against boron thanks
608 to the higher cross-linking degree of its polyamide rejection layer. Greater improvements in
609 selectivity were observed for NaCl and a hydrophobic EDC propylparaben due to enhanced
610 Donnan exclusion and suppressed hydrophobic interaction, respectively, in addition to the
611 size exclusion effect. The inclusion of porous materials^{96, 97, 281} and coating layers^{98, 99, 247}
612 with intrinsically high selectivity against target solutes are also of great potential.
613 Furthermore, improving solute/solute selectivity²⁷⁶ could be another sweet spot for the future
614 development of TFNi membranes, e.g., Cl⁻/SO₄²⁻ selectivity for the treatment of cooling
615 tower water and paper mills wastewater,^{221, 260, 261} dye/salt selectivity in textile wastewater
616 treatment,^{227-230, 270} Li⁺/Mg²⁺ selectivity for lithium extraction from salt lake water.²²⁵

617

618 ■ CONCLUDING REMARKS AND FUTURE PERSPECTIVES

619 This review provides the state of the art of TFNi membranes in terms of materials,
620 mechanisms, and separation performance. The relevant environmental applications are
621 assessed with respect to potential savings in energy consumptions and process efficiency on
622 the basis of membrane water permeance and selectivity. In general, TFNi membranes offer
623 great potential for simultaneous enhancements in both water permeance and solute selectivity.
624 Significant energy savings (e.g., up to 80%) is possible for feed waters with low osmotic
625 pressure (e.g., water reuse). In contrast, only marginal reduction in SEC is expected for
626 SWRO since its SEC is largely dictated by the high osmotic pressure of seawater. The
627 existing literature seems to have mainly focused on the removal of simple salts, yet there is a
628 lack of systematic studies on other important contaminants that are critical for certain
629 environmental applications (Table 3). Future studies should extend TFNi membranes to a
630 wider selection of solutes and investigate their solute/water and solute/solute selectivity to
631 fully unleash their potential. Furthermore, although the review has focused primarily on RO
632 and NF processes, the mechanisms involved and application constraints are also relevant to
633 other membrane processes such as FO.^{282, 283} Compared to RO and NF, the applications of
634 TFNi membranes for FO process could offer additional benefits. For example, the inclusion
635 of a hydrophilic interlayer could greatly reduce the structural parameter (*S* value) of the TFNi
636 FO membranes.^{117, 136} This could be possibly explained by the elimination of PA inside
637 substrate pore that not only reduces the overall membrane hydraulic resistance but also
638 mitigates internal concentration polarization.¹¹⁷ In addition, the significantly improved
639 selectivity of TFNi membranes (Figure 2), originated from reduced defects formation^{121, 122}
640 and/or enhanced crosslinking degree^{57, 153} of its polyamide rejection layer, could further
641 reduce the specific salt flux in the FO process.¹²⁴ As a result of these beneficial effects, TFNi
642 membranes can potentially offer nearly an order of magnitude improvement in FO water flux
643 together reduced reverse solute flux.^{117, 124}

644

645 In view of the greatly enhanced separation performance of TFNi membranes over their

646 conventional TFN counterparts and the fact that several TFN membranes have also been
647 successfully commercialized,⁴⁷⁻⁴⁹ it is reasonable to expect the potential commercialization of
648 TFNi membranes in the near future. However, several critical issues need to be thoroughly
649 addressed, including costs, long-term membrane stability, and risks of nanomaterials leaching.
650 Based on these considerations, the dip coating method may be the most practical way for the
651 preparation of interlayers in view of its relatively low cost and its existing use in commercial
652 membrane production lines (e.g., PVA coating in RO post-treatment).¹⁸⁹⁻¹⁹¹

653

654 In view of the important gutter effect on the transport paths in TFNi membranes, more
655 modelling and experimental works are needed to systematically evaluate the effect of
656 interlayer properties (e.g., thickness, permeability, continuous coatings vs. discrete nanofillers,
657 etc.) on both water permeance and selectivity. One interesting aspect for future research is to
658 explore the use of specific chemistry of interlayer materials for improving the selectivity
659 against target contaminants.^{98, 99, 247} Furthermore, advanced membrane characterization
660 techniques (e.g., QCM-D^{57, 121}, Rutherford backscattering spectrometry,^{284, 285}
661 electrochemical impedance spectroscopy,^{286, 287} positron annihilation lifetime spectroscopy,^{288,}
662 ²⁸⁹, 3D TEM tomography^{290, 291} and etc.^{146, 154, 292, 293}) are needed. Such advanced
663 characterization can provide better understanding of the effect of interlayers on the
664 physiochemical properties of polyamide layers, particularly with respect to the
665 orientation/pattern of nanofillers, their interactions with the rejection layer and substrate, their
666 effect on the transport behavior and the overall membrane integrity,^{7, 142, 214, 215} which are
667 critical issues for many membrane applications.

668

669 Despite the great enhancement effect in membrane permeability and selectivity, there have
670 been only a handful studies on the fouling and chlorine resistance of TFNi membranes. For
671 some TFNi membranes, the slower/controlled release of amine monomers can result in
672 smoother membrane surfaces (Table 2),^{55, 68} which tends to mitigate membrane fouling.⁶⁸
673 Although TFNi membranes incorporating biocidal agents (e.g., AgNPs) can still achieve

674 some antimicrobial and antibiofouling properties via non-contact killing,⁷¹ the embedding of
675 such materials underneath the polyamide would inhibit the direct killing mechanism that is
676 often utilized in surface-laden TFN membranes (e.g., by coating biocidal agents on a TFC
677 membrane surface¹³⁴). Nevertheless, the additional coating layer in the latter case could
678 adversely affect membrane hydraulic resistance,¹⁰ resulting in reduced water permeance.^{10, 98}
679 An interesting opportunity exists to achieve better antifouling performance for TFNi
680 membranes. The inclusion of an interlayer changes the water transport path in the polyamide
681 layer towards a more uniform distribution (Figure 4b). This could potentially eliminate hot
682 spots of extremely high localized flux (e.g., directly over the substrate pores in Figure 4a¹³⁸)
683 and thereby reducing the membrane fouling tendency.²⁹⁴ Some recent studies have also
684 demonstrated the possibility of interlayer materials for improving chlorine resistance, e.g., by
685 the inhibition of N-chlorination and ring-chlorination,^{14, 186} resulting in improved membrane
686 chlorine resistance.¹⁸⁶ Future studies need to perform more systematic evaluation on the
687 fouling and chlorine resistance to enable a wide range of real applications.^{13, 295-297}

688 ■ **ASSOCIATED CONTENT**

689 The Supporting Information is available free of charge on the ACS Publications website at

690 DOI:

691 S1. Summary of materials, fabrication methods and separation performances of TFNi
692 membranes; S2. Calculations of specific energy consumption

693

694 ■ **AUTHOR INFORMATION**

695 *To whom all correspondence should be addressed.

696 Tel: +852 2859 1976, E-mail address: tangc@hku.hk

697 Tel: +852 2857 8470, E-mail address: zheyang@connect.hku.hk

698

699 **Author Contributions**

700 ¹These authors contributed equally to this work.

701

702 **Notes**

703 The authors declare no competing financial interest.

704

705 ■ **ACKNOWLEDGEMENTS**

706 The work described in this paper was partially supported by a grant from the Research Grants
707 Council of the Hong Kong Special Administration Region, China (C7051-17G). We also
708 appreciate the Seed Funding for Basic Research Scheme of the University of Hong Kong.

709

710 ■ REFERENCES

- 711 1. Seckler, D.; Barker, R.; Amarasinghe, U., Water scarcity in the twenty-first century. *Int. J.*
712 *Water Res. Dev.* **1999**, *15*, (1-2), 29-42.
- 713 2. Elimelech, M.; Phillip, W. A., The future of seawater desalination: energy, technology,
714 and the environment. *Science* **2011**, *333*, (6043), 712-717.
- 715 3. Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Marinas, B. J.; Mayes, A.
716 M., Science and technology for water purification in the coming decades. *Nature* **2008**, *452*,
717 (7185), 301-311.
- 718 4. Mekonnen, M. M.; Hoekstra, A. Y., Four billion people facing severe water scarcity. *Sci.*
719 *Adv.* **2016**, *2*, (2), e1500323.
- 720 5. Lee, K. P.; Arnot, T. C.; Mattia, D., A review of reverse osmosis membrane materials for
721 desalination—development to date and future potential. *J. Membr. Sci.* **2011**, *370*, (1), 1-22.
- 722 6. Yang, Z.; Ma, X.-H.; Tang, C. Y., Recent development of novel membranes for
723 desalination. *Desalination* **2018**, *434*, 37-59.
- 724 7. Tang, C. Y.; Yang, Z.; Guo, H.; Wen, J.; Nghiem, L. D.; Cornelissen, E. R., Potable water
725 reuse through advanced membrane technology. *Environ. Sci. Technol.* **2018**, *52*, (18),
726 10215-10223.
- 727 8. Li, D.; Yan, Y.; Wang, H., Recent advances in polymer and polymer composite
728 membranes for reverse and forward osmosis processes. *Prog. Polym. Sci.* **2016**, *61*, 104-155.
- 729 9. Li, D.; Wang, H., Recent developments in reverse osmosis desalination membranes. *J.*
730 *Mater. Chem.* **2010**, *20*, (22), 4551-4566.
- 731 10. Yang, Z.; Guo, H.; Tang, C. Y., The upper bound of thin-film composite (TFC)
732 polyamide membranes for desalination. *J. Membr. Sci.* **2019**, *590*, 117297.
- 733 11. Geise, G. M.; Park, H. B.; Sagle, A. C.; Freeman, B. D.; McGrath, J. E., Water
734 permeability and water/salt selectivity tradeoff in polymers for desalination. *J. Membr. Sci.*
735 **2011**, *369*, (1), 130-138.
- 736 12. Werber, J. R.; Osuji, C. O.; Elimelech, M., Materials for next-generation desalination and
737 water purification membranes. *Nature. Rev. Mater.* **2016**, *1*, 16018.
- 738 13. She, Q.; Wang, R.; Fane, A. G.; Tang, C. Y., Membrane fouling in osmotically driven
739 membrane processes: A review. *J. Membr. Sci.* **2016**, *499*, 201-233.
- 740 14. Do, V. T.; Tang, C. Y.; Reinhard, M.; Leckie, J. O., Effects of chlorine exposure
741 conditions on physiochemical properties and performance of a polyamide membrane
742 Mechanisms and implications. *Environ. Sci. Technol.* **2012**, *46*, (24), 13184-13192.
- 743 15. Tang, C.; Wang, Z.; Petrinić, I.; Fane, A. G.; Hélix-Nielsen, C., Biomimetic aquaporin
744 membranes coming of age. *Desalination* **2015**, *368*, 89-105.
- 745 16. Yin, J.; Deng, B., Polymer-matrix nanocomposite membranes for water treatment. *J.*
746 *Membr. Sci.* **2015**, *479*, 256-275.
- 747 17. Jeong, B.-H.; Hoek, E. M.; Yan, Y.; Subramani, A.; Huang, X.; Hurwitz, G.; Ghosh, A.
748 K.; Jawor, A., Interfacial polymerization of thin film nanocomposites: a new concept for
749 reverse osmosis membranes. *J. Membr. Sci.* **2007**, *294*, (1), 1-7.
- 750 18. Yin, J.; Kim, E.-S.; Yang, J.; Deng, B., Fabrication of a novel thin-film nanocomposite

751 (TFN) membrane containing MCM-41 silica nanoparticles (NPs) for water purification. *J.*
752 *Membr. Sci.* **2012**, *423*, 238-246.

753 19. Dong, H.; Zhao, L.; Zhang, L.; Chen, H.; Gao, C.; Winston Ho, W. S., High-flux reverse
754 osmosis membranes incorporated with NaY zeolite nanoparticles for brackish water
755 desalination. *J. Membr. Sci.* **2015**, *476*, 373-383.

756 20. Safarpour, M.; Vatanpour, V.; Khataee, A.; Esmaeili, M., Development of a novel high
757 flux and fouling-resistant thin film composite nanofiltration membrane by embedding
758 reduced graphene oxide/TiO₂. *Sep. Purif. Technol.* **2015**, *154*, 96-107.

759 21. Zhao, F. Y.; Ji, Y. L.; Weng, X. D.; Mi, Y. F.; Ye, C. C.; An, Q. F.; Gao, C. J., High-Flux
760 Positively Charged Nanocomposite Nanofiltration Membranes Filled with Poly(dopamine)
761 Modified Multiwall Carbon Nanotubes. *ACS Appl. Mater. Interfaces* **2016**, *8*, (10),
762 6693-6700.

763 22. Guo, X.; Liu, D.; Han, T.; Huang, H.; Yang, Q.; Zhong, C., Preparation of thin film
764 nanocomposite membranes with surface modified MOF for high flux organic solvent
765 nanofiltration. *AIChE Journal* **2017**, *63*, (4), 1303-1312.

766 23. Ma, D.; Peh, S. B.; Han, G.; Chen, S. B., Thin-Film Nanocomposite (TFN) Membranes
767 Incorporated with Super-Hydrophilic Metal-Organic Framework (MOF) UiO-66: Toward
768 Enhancement of Water Flux and Salt Rejection. *ACS Appl. Mater. Interfaces* **2017**, *9*, (8),
769 7523-7534.

770 24. Wu, M.; Ma, T.; Su, Y.; Wu, H.; You, X.; Jiang, Z.; Kasher, R., Fabrication of composite
771 nanofiltration membrane by incorporating attapulgite nanorods during interfacial
772 polymerization for high water flux and antifouling property. *J. Membr. Sci.* **2017**, *544*, 79-87.

773 25. Zhang, C.; Wei, K.; Zhang, W.; Bai, Y.; Sun, Y.; Gu, J., Graphene Oxide Quantum Dots
774 Incorporated into a Thin Film Nanocomposite Membrane with High Flux and Antifouling
775 Properties for Low-Pressure Nanofiltration. *ACS Appl. Mater. Interfaces* **2017**, *9*, (12),
776 11082-11094.

777 26. Zheng, J.; Li, M.; Yu, K.; Hu, J.; Zhang, X.; Wang, L., Sulfonated multiwall carbon
778 nanotubes assisted thin-film nanocomposite membrane with enhanced water flux and
779 anti-fouling property. *J. Membr. Sci.* **2017**, *524*, 344-353.

780 27. Gao, X.; Li, Y.; Yang, X.; Shang, Y.; Wang, Y.; Gao, B.; Wang, Z., Highly permeable and
781 antifouling reverse osmosis membranes with acidified graphitic carbon nitride nanosheets as
782 nanofillers. *J. Mater. Chem. A* **2017**, *5*, (37), 19875-19883.

783 28. Ghaemi, N., Novel antifouling nano-enhanced thin-film composite membrane containing
784 cross-linkable acrylate-alumoxane nanoparticles for water softening. *J. Colloid. Interface Sci.*
785 **2017**, *485*, 81-90.

786 29. Ma, R.; Ji, Y. L.; Guo, Y. S.; Mi, Y. F.; An, Q. F.; Gao, C. J., Fabrication of antifouling
787 reverse osmosis membranes by incorporating zwitterionic colloids nanoparticles for brackish
788 water desalination. *Desalination* **2017**, *416*, 35-44.

789 30. Wang, J.; Wang, Y.; Zhu, J.; Zhang, Y.; Liu, J.; Van der Bruggen, B., Construction of
790 TiO₂@graphene oxide incorporated antifouling nanofiltration membrane with elevated
791 filtration performance. *J. Membr. Sci.* **2017**, *533*, 279-288.

792 31. Zirehpour, A.; Rahimpour, A.; Arabi Shamsabadi, A.; Sharifian, M. G.; Soroush, M.,

793 Mitigation of Thin-Film Composite Membrane Biofouling via Immobilizing Nano-Sized
794 Biocidal Reservoirs in the Membrane Active Layer. *Environ. Sci. Technol.* **2017**, *51*, (10),
795 5511-5522.

796 32. Abdikheibari, S.; Lei, W.; Dumée, L. F.; Milne, N.; Baskaran, K., Thin film
797 nanocomposite nanofiltration membranes from amine functionalized-boron
798 nitride/polypiperazine amide with enhanced flux and fouling resistance. *J. Mater. Chem. A*
799 **2018**, *6*, (25), 12066-12081.

800 33. Bai, L.; Liu, Y.; Bossa, N.; Ding, A.; Ren, N.; Li, G.; Liang, H.; Wiesner, M. R.,
801 Incorporation of Cellulose Nanocrystals (CNCs) into the Polyamide Layer of Thin-Film
802 Composite (TFC) Nanofiltration Membranes for Enhanced Separation Performance and
803 Antifouling Properties. *Environ. Sci. Technol.* **2018**, *52*, (19), 11178-11187.

804 34. Bi, R.; Zhang, Q.; Zhang, R.; Su, Y.; Jiang, Z., Thin film nanocomposite membranes
805 incorporated with graphene quantum dots for high flux and antifouling property. *J. Membr.*
806 *Sci.* **2018**, *553*, 17-24.

807 35. Jeon, S.; Park, C. H.; Park, S. H.; Shin, M. G.; Kim, H. J.; Baek, K. Y.; Chan, E. P.; Bang,
808 J.; Lee, J. H., Star polymer-assembled thin film composite membranes with high separation
809 performance and low fouling. *J. Membr. Sci.* **2018**, *555*, 369-378.

810 36. Buonomenna, M. G., Nano-enhanced reverse osmosis membranes. *Desalination* **2013**,
811 *314*, 73-88.

812 37. Lau, W.; Gray, S.; Matsuura, T.; Emadzadeh, D.; Chen, J. P.; Ismail, A., A review on
813 polyamide thin film nanocomposite (TFN) membranes: History, applications, challenges and
814 approaches. *Water Res.* **2015**, *80*, 306-324.

815 38. Esfahani, M. R.; Aktij, S. A.; Dabaghian, Z.; Firouzjaei, M. D.; Rahimpour, A.; Eke, J.;
816 Escobar, I. C.; Abolhassani, M.; Greenlee, L. F.; Esfahani, A. R., Nanocomposite membranes
817 for water separation and purification: Fabrication, modification, and applications. *Sep. Purif.*
818 *Technol.* **2018**, *213*, 465-499.

819 39. Pendergast, M. T. M.; Nygaard, J. M.; Ghosh, A. K.; Hoek, E. M. V., Using
820 nanocomposite materials technology to understand and control reverse osmosis membrane
821 compaction. *Desalination* **2010**, *261*, (3), 255-263.

822 40. Pendergast, M. M.; Ghosh, A. K.; Hoek, E. M. V., Separation performance and interfacial
823 properties of nanocomposite reverse osmosis membranes. *Desalination* **2013**, *308*, 180-185.

824 41. Ma, N.; Wei, J.; Qi, S.; Zhao, Y.; Gao, Y.; Tang, C. Y., Nanocomposite substrates for
825 controlling internal concentration polarization in forward osmosis membranes. *J. Membr. Sci.*
826 **2013**, *441*, 54-62.

827 42. Emadzadeh, D.; Lau, W.; Ismail, A., Synthesis of thin film nanocomposite forward
828 osmosis membrane with enhancement in water flux without sacrificing salt rejection.
829 *Desalination* **2013**, *330*, 90-99.

830 43. Wang, Y.; Ou, R.; Ge, Q.; Wang, H.; Xu, T., Preparation of polyethersulfone/carbon
831 nanotube substrate for high-performance forward osmosis membrane. *Desalination* **2013**, *330*,
832 70-78.

833 44. Son, M.; Choi, H.-g.; Liu, L.; Celik, E.; Park, H.; Choi, H., Efficacy of carbon nanotube
834 positioning in the polyethersulfone support layer on the performance of thin-film composite

835 membrane for desalination. *Chem. Eng. J.* **2015**, *266*, 376-384.

836 45. Tian, M.; Wang, Y.-N.; Wang, R., Synthesis and characterization of novel
837 high-performance thin film nanocomposite (TFN) FO membranes with nanofibrous substrate
838 reinforced by functionalized carbon nanotubes. *Desalination* **2015**, *370*, 79-86.

839 46. Park, M. J.; Phuntsho, S.; He, T.; Nisola, G. M.; Tijing, L. D.; Li, X.-M.; Chen, G.;
840 Chung, W.-J.; Shon, H. K., Graphene oxide incorporated polysulfone substrate for the
841 fabrication of flat-sheet thin-film composite forward osmosis membranes. *J. Membr. Sci.*
842 **2015**, *493*, 496-507.

843 47. <https://aquaporin.com/>.

844 48. <http://www.lgwatersolutions.com/en/product/seawater-ro>.

845 49. <http://www.lgwatersolutions.com/en/product/brackish-water-ro>.

846 50. Liu, X.; Ng, H. Y., Fabrication of layered silica-polysulfone mixed matrix substrate
847 membrane for enhancing performance of thin-film composite forward osmosis membrane. *J.*
848 *Membr. Sci.* **2015**, *481*, 148-163.

849 51. Lee, J.-Y.; Wang, Y.; Tang, C. Y.; Huo, F., Mesoporous Silica Gel-Based Mixed Matrix
850 Membranes for Improving Mass Transfer in Forward Osmosis: Effect of Pore Size of Filler.
851 *Sci. Rep.* **2015**, *5*, 16808.

852 52. Yin, J.; Zhu, G.; Deng, B., Graphene oxide (GO) enhanced polyamide (PA) thin-film
853 nanocomposite (TFN) membrane for water purification. *Desalination* **2016**, *379*, 93-101.

854 53. Yang, Z.; Yin, J.; Deng, B., Enhancing water flux of thin-film nanocomposite (TFN)
855 membrane by incorporation of bimodal silica nanoparticles. *Aims Press Environ. Sci.* **2016**, *3*,
856 (2), 185-198.

857 54. Wu, H.; Tang, B.; Wu, P., Optimizing polyamide thin film composite membrane
858 covalently bonded with modified mesoporous silica nanoparticles. *J. Membr. Sci.* **2013**, *428*,
859 341-348.

860 55. Karan, S.; Jiang, Z.; Livingston, A. G., Sub-10 nm polyamide nanofilms with ultrafast
861 solvent transport for molecular separation. *Science* **2015**, *348*, (6241), 1347-1351.

862 56. Liu, X.-W.; Cao, Y.; Li, Y.-X.; Xu, Z.-L.; Li, Z.; Wang, M.; Ma, X.-H., High-performance
863 polyamide/ceramic hollow fiber TFC membranes with TiO₂ interlayer for pervaporation
864 dehydration of isopropanol solution. *J. Membr. Sci.* **2019**, *576*, 26-35.

865 57. Yang, Z.; Guo, H.; Yao, Z.-k.; Mei, Y.; Tang, C. Y., Hydrophilic Silver Nanoparticles
866 Induce Selective Nanochannels in Thin Film Nanocomposite Polyamide Membranes. *Environ.*
867 *Sci. Technol.* **2019**, *53*, (9), 5301-5308.

868 58. Chan, W.-F.; Marand, E.; Martin, S. M., Novel zwitterion functionalized carbon nanotube
869 nanocomposite membranes for improved RO performance and surface anti-biofouling
870 resistance. *J. Membr. Sci.* **2016**, *509*, 125-137.

871 59. Gao, S.; Zhu, Y.; Gong, Y.; Wang, Z.; Fang, W.; Jin, J., Ultrathin Polyamide
872 Nanofiltration Membrane Fabricated on Brush-Painted Single-Walled Carbon Nanotube
873 Network Support for Ion Sieving. *ACS Nano* **2019**, *13*, (5), 5278-5290.

874 60. Zhao, X.; Li, J.; Liu, C., A novel TFC-type FO membrane with inserted sublayer of
875 carbon nanotube networks exhibiting the improved separation performance. *Desalination*
876 **2017**, *413*, 176-183.

- 877 61. Choi, H.-g.; Shah, A. A.; Nam, S.-E.; Park, Y.-I.; Park, H., Thin-film composite
878 membranes comprising ultrathin hydrophilic polydopamine interlayer with graphene oxide
879 for forward osmosis. *Desalination* **2019**, *449*, 41-49.
- 880 62. Shi, J.; Wu, W.; Xia, Y.; Li, Z.; Li, W., Confined interfacial polymerization of
881 polyamide-graphene oxide composite membranes for water desalination. *Desalination* **2018**,
882 *441*, 77-86.
- 883 63. Sarango, L.; Pasetta, L.; Navarro, M.; Zornoza, B.; Coronas, J., Controlled deposition of
884 MOFs by dip-coating in thin film nanocomposite membranes for organic solvent
885 nanofiltration. *J. Ind. Eng. Chem.* **2018**, *59*, 8-16.
- 886 64. Van Goethem, C.; Verbeke, R.; Hermans, S.; Bernstein, R.; Vankelecom, I. F. J.,
887 Controlled positioning of MOFs in interfacially polymerized thin-film nanocomposites. *J.*
888 *Mater. Chem. A* **2016**, *4*, (42), 16368-16376.
- 889 65. Zhu, J.; Hou, J.; Yuan, S.; Zhao, Y.; Li, Y.; Zhang, R.; Tian, M.; Li, J.; Wang, J.; Van der
890 Bruggen, B., MOFs-positioned polyamide membrane with fishnet-like structure for elevated
891 nanofiltration performance. *J. Mater. Chem. A* **2019**, *7*, (27), 16313-16322.
- 892 66. Wen, Y.; Zhang, X.; Li, X.; Wang, Z.; Tang, C. Y., Metal–Organic Framework
893 Nanosheets for Thin-Film Composite Membranes with Enhanced Permeability and
894 Selectivity. *ACS Applied Nano Materials* **2020**, *3*, (9), 9238-9248.
- 895 67. Li, Y.; Su, Y.; Li, J.; Zhao, X.; Zhang, R.; Fan, X.; Zhu, J.; Ma, Y.; Liu, Y.; Jiang, Z.,
896 Preparation of thin film composite nanofiltration membrane with improved structural stability
897 through the mediation of polydopamine. *J. Membr. Sci.* **2015**, *476*, 10-19.
- 898 68. Choi, W.; Jeon, S.; Kwon, S. J.; Park, H.; Park, Y.-I.; Nam, S.-E.; Lee, P. S.; Lee, J. S.;
899 Choi, J.; Hong, S.; Chan, E. P.; Lee, J.-H., Thin film composite reverse osmosis membranes
900 prepared via layered interfacial polymerization. *J. Membr. Sci.* **2017**, *527*, 121-128.
- 901 69. Yang, X.; Du, Y.; Zhang, X.; He, A.; Xu, Z.-K., Nanofiltration Membrane with a
902 Mussel-Inspired Interlayer for Improved Permeation Performance. *Langmuir* **2017**, *33*, (9),
903 2318-2324.
- 904 70. Zhai, Z.; Zhao, N.; Dong, W.; Li, P.; Sun, H.; Niu, Q. J., In Situ Assembly of a Zeolite
905 Imidazolate Framework Hybrid Thin-Film Nanocomposite Membrane with Enhanced
906 Desalination Performance Induced by Noria-Polyethyleneimine Codeposition. *ACS Appl.*
907 *Mater. Interfaces* **2019**, *11*, (13), 12871-12879.
- 908 71. Yang, Z.; Wu, Y.; Guo, H.; Ma, X.-H.; Lin, C.-E.; Zhou, Y.; Cao, B.; Zhu, B.-K.; Shih, K.;
909 Tang, C. Y., A novel thin-film nano-templated composite membrane with in situ silver
910 nanoparticles loading: Separation performance enhancement and implications. *J. Membr. Sci.*
911 **2017**, *544*, 351-358.
- 912 72. Akther, N.; Phuntsho, S.; Chen, Y.; Ghaffour, N.; Shon, H. K., Recent advances in
913 nanomaterial-modified polyamide thin-film composite membranes for forward osmosis
914 processes. *J. Membr. Sci.* **2019**, *584*, 20-45.
- 915 73. Zhao, D. L.; Japip, S.; Zhang, Y.; Weber, M.; Maletzko, C.; Chung, T.-S., Emerging
916 thin-film nanocomposite (TFN) membranes for reverse osmosis: A review. *Water Res.* **2020**,
917 *173*, 115557.
- 918 74. Huang, Y.; Jin, H.; Yu, P.; Luo, Y., Polyamide thin-film composite membrane based on

919 nano-silica modified polysulfone microporous support layer for forward osmosis.
920 *Desalination Water Treat.* **2016**, *57*, (43), 20177-20187.

921 75. Pan, S.-F.; Ke, X.-X.; Wang, T.-Y.; Liu, Q.; Zhong, L.-B.; Zheng, Y.-M., Synthesis of
922 Silver Nanoparticles Embedded Electrospun PAN Nanofiber Thin-Film Composite Forward
923 Osmosis Membrane to Enhance Performance and Antimicrobial Activity. *Ind. Eng. Chem.*
924 *Res.* **2019**, *58*, (2), 984-993.

925 76. Emadzadeh, D.; Lau, W. J.; Matsuura, T.; Ismail, A. F.; Rahbari-Sisakht, M., Synthesis
926 and characterization of thin film nanocomposite forward osmosis membrane with hydrophilic
927 nanocomposite support to reduce internal concentration polarization. *J. Membr. Sci.* **2014**,
928 *449*, 74-85.

929 77. Emadzadeh, D.; Lau, W. J.; Matsuura, T.; Rahbari-Sisakht, M.; Ismail, A. F., A novel thin
930 film composite forward osmosis membrane prepared from PSf-TiO₂ nanocomposite
931 substrate for water desalination. *Chem. Eng. J.* **2014**, *237*, 70-80.

932 78. Ramezani Darabi, R.; Jahanshahi, M.; Peyravi, M., A support assisted by photocatalytic
933 Fe₃O₄/ZnO nanocomposite for thin-film forward osmosis membrane. *Chem. Eng. Res. Des.*
934 **2018**, *133*, 11-25.

935 79. Zhao, Q.; Zhao, D. L.; Chung, T. S., Nanoclays - Incorporated Thin - Film
936 Nanocomposite Membranes for Reverse Osmosis Desalination. *Adv. Mater. Interfaces* **2020**,
937 *7*, (8), 1902108.

938 80. Lind, M. L.; Ghosh, A. K.; Jawor, A.; Huang, X.; Hou, W.; Yang, Y.; Hoek, E. M. V.,
939 Influence of zeolite crystal size on zeolite-polyamide thin film nanocomposite membranes.
940 *Langmuir* **2009**, *25*, (17), 10139-10145.

941 81. Yin, J.; Yang, Z.; Tang, C. Y.; Deng, B., Probing the Contributions of Interior and
942 Exterior Channels of Nanofillers towards Enhanced Separation Performance of Thin-Film
943 Nanocomposite Reverse Osmosis Membrane. *Environ. Sci. Technol. Lett.* **2020**.

944 82. Kadhom, M.; Deng, B., Metal-organic frameworks (MOFs) in water filtration
945 membranes for desalination and other applications. *Appl. Mater. Today* **2018**, *11*, 219-230.

946 83. Sorribas, S.; Gorgojo, P.; Téllez, C.; Coronas, J.; Livingston, A. G., High flux thin film
947 nanocomposite membranes based on metal-organic frameworks for organic solvent
948 nanofiltration. *J. Am. Chem. Soc.* **2013**, *135*, (40), 15201-15208.

949 84. Zhao, D. L.; Yeung, W. S.; Zhao, Q.; Chung, T.-S., Thin-film nanocomposite membranes
950 incorporated with UiO-66-NH₂ nanoparticles for brackish water and seawater desalination. *J.*
951 *Membr. Sci.* **2020**, *604*, 118039.

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

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

958 87. Qi, S.; Wang, R.; Chaitra, G. K. M.; Torres, J.; Hu, X.; Fane, A. G., Aquaporin-based
959 biomimetic reverse osmosis membranes: Stability and long term performance. *J. Membr. Sci.*
960 **2016**, *508*, 94-103.

- 961 88. Zhao, Y.; Qiu, C.; Li, X.; Vararattanavech, A.; Shen, W.; Torres, J.; Helix-Nielsen, C.;
962 Wang, R.; Hu, X.; Fane, A. G., Synthesis of robust and high-performance aquaporin-based
963 biomimetic membranes by interfacial polymerization-membrane preparation and RO
964 performance characterization. *J. Membr. Sci.* **2012**, *423*, 422-428.
- 965 89. Barboiu, M., Artificial water channels. *Angew. Chem.* **2012**, *51*, (47), 11674-11676.
- 966 90. Yang, Z.; Huang, X.; Ma, X.-h.; Zhou, Z.-w.; Guo, H.; Yao, Z.; Feng, S.-P.; Tang, C. Y.,
967 Fabrication of a novel and green thin-film composite membrane containing nanovoids for
968 water purification. *J. Membr. Sci.* **2019**, *570-571*, 314-321.
- 969 91. Ma, X.-H.; Yao, Z.; Yang, Z.; Guo, H.; Xu, Z.; Tang, C. Y.; Elimelech, M., Nanofoaming
970 of Polyamide Desalination Membranes to Tune Permeability and Selectivity. *Environ. Sci.*
971 *Technol. Lett.* **2018**, *5*, (2), 123-130.
- 972 92. Ma, X.; Yang, Z.; Yao, Z.; Guo, H.; Xu, Z.; Tang, C. Y., Tuning roughness features of
973 thin film composite polyamide membranes for simultaneously enhanced permeability,
974 selectivity and anti-fouling performance. *J. Colloid. Interface Sci.* **2019**, *540*, 382-388.
- 975 93. Shen, L.; Hung, W.-s.; Zuo, J.; Zhang, X.; Lai, J.-Y.; Wang, Y., High-performance
976 thin-film composite polyamide membranes developed with green ultrasound-assisted
977 interfacial polymerization. *J. Membr. Sci.* **2019**, *570-571*, 112-119.
- 978 94. Tang, C.; Zhao, Y.; Wang, R.; Helix-Nielsen, C.; Fane, A., Desalination by biomimetic
979 aquaporin membranes: Review of status and prospects. *Desalination* **2013**, *308*, 34-40.
- 980 95. Kim, E. S.; Hwang, G.; Gamal El-Din, M.; Liu, Y., Development of nanosilver and
981 multi-walled carbon nanotubes thin-film nanocomposite membrane for enhanced water
982 treatment. *J. Membr. Sci.* **2012**, *394-395*, 37-48.
- 983 96. Dai, R.; Wang, X.; Tang, C. Y.; Wang, Z., Dually Charged MOF-Based Thin-Film
984 Nanocomposite Nanofiltration Membrane for Enhanced Removal of Charged
985 Pharmaceutically Active Compounds. *Environ. Sci. Technol.* **2020**, *54*, (12), 7619-7628.
- 986 97. Dai, R.; Guo, H.; Tang, C. Y.; Chen, M.; Li, J.; Wang, Z., Hydrophilic Selective
987 Nanochannels Created by Metal Organic Frameworks in Nanofiltration Membranes Enhance
988 Rejection of Hydrophobic Endocrine-Disrupting Compounds. *Environ. Sci. Technol.* **2019**, *53*,
989 (23), 13776-13783.
- 990 98. Guo, H.; Deng, Y.; Tao, Z.; Yao, Z.; Wang, J.; Lin, C.; Zhang, T.; Zhu, B.; Tang, C. Y.,
991 Does Hydrophilic Polydopamine Coating Enhance Membrane Rejection of Hydrophobic
992 Endocrine-Disrupting Compounds? *Environ. Sci. & Technol. Lett.* **2016**, *3*, (9), 332-338.
- 993 99. Guo, H.; Yao, Z.; Yang, Z.; Ma, X.; Wang, J.; Tang, C. Y., A one-step rapid assembly of
994 thin film coating using green coordination complexes for enhanced removal of trace organic
995 contaminants by membranes. *Environ. Sci. Technol.* **2017**, *51*, (21), 12638-12643.
- 996 100. Lee, J.-Y.; Tang, C. Y.; Huo, F., Fabrication of Porous Matrix Membrane (PMM)
997 Using Metal-Organic Framework as Green Template for Water Treatment. *Sci. Rep.* **2014**, *4*,
998 (1), 3740.
- 999 101. Lee, J.-Y.; She, Q.; Huo, F.; Tang, C. Y., Metal-organic framework-based porous
1000 matrix membranes for improving mass transfer in forward osmosis membranes. *J. Membr. Sci.*
1001 **2015**, *492*, 392-399.
- 1002 102. Lu, P.; Wang, Y.; Wang, L.; Wei, Y.; Li, W.; Li, Y.; Tang, C. Y., Immobilization of

1003 sulfonated polysulfone via 2D LDH nanosheets during phase-inversion: A novel strategy
1004 towards greener membrane synthesis and enhanced desalination performance. *J. Membr. Sci.*
1005 **2020**, *614*, 118508.

1006 103. Pal, A.; Dey, T. K.; Singhal, A.; Bindal, R. C.; Tewari, P. K., Nano-ZnO impregnated
1007 inorganic-polymer hybrid thinfilm nanocomposite nanofiltration membranes: An
1008 investigation of variation in structure, morphology and transport properties. *RSC Adv.* **2015**, *5*,
1009 (43), 34134-34151.

1010 104. Ang, M. B. M. Y.; Trilles, C. A.; De Guzman, M. R.; Pereira, J. M.; Aquino, R. R.;
1011 Huang, S.-H.; Hu, C.-C.; Lee, K.-R.; Lai, J.-Y., Improved performance of thin-film
1012 nanocomposite nanofiltration membranes as induced by embedded polydopamine-coated
1013 silica nanoparticles. *Sep. Purif. Technol.* **2019**, *224*, 113-120.

1014 105. Niksefat, N.; Jahanshahi, M.; Rahimpour, A., The effect of SiO₂ nanoparticles on
1015 morphology and performance of thin film composite membranes for forward osmosis
1016 application. *Desalination* **2014**, *343*, 140-146.

1017 106. Al Mayyahi, A., TiO₂ polyamide thin film nanocomposite reverses osmosis
1018 membrane for water desalination. *Membranes* **2018**, *8*, (3), 66.

1019 107. Lee, H. S.; Im, S. J.; Kim, J. H.; Kim, H. J.; Kim, J. P.; Min, B. R. J. D., Polyamide
1020 thin-film nanofiltration membranes containing TiO₂ nanoparticles. *Desalination* **2008**, *219*,
1021 (1-3), 48-56.

1022 108. Xue, S.-M.; Xu, Z.-L.; Tang, Y.-J.; Ji, C.-H., Polypiperazine-amide Nanofiltration
1023 Membrane Modified by Different Functionalized Multiwalled Carbon Nanotubes (MWCNTs).
1024 *ACS Appl. Mater. Interfaces* **2016**, *8*, (29), 19135-19144.

1025 109. Ma, X.-H.; Guo, H.; Yang, Z.; Yao, Z.-K.; Qing, W.-H.; Chen, Y.-L.; Xu, Z.-L.; Tang,
1026 C. Y., Carbon nanotubes enhance permeability of ultrathin polyamide rejection layers. *J.*
1027 *Membr. Sci.* **2019**, *570-571*, 139-145.

1028 110. Yao, Z.; Guo, H.; Yang, Z.; Qing, W.; Tang, C. Y., Preparation of nanocavity-contained
1029 thin film composite nanofiltration membranes with enhanced permeability and divalent to
1030 monovalent ion selectivity. *Desalination* **2018**, *445*, 115-122.

1031 111. Rastgar, M.; Shakeri, A.; Bozorg, A.; Salehi, H.; Saadattalab, V., Impact of nanoparticles
1032 surface characteristics on pore structure and performance of forward osmosis membranes.
1033 *Desalination* **2017**, *421*, 179-189.

1034 112. Emadzadeh, D.; Lau, W.; Matsuura, T.; Hilal, N.; Ismail, A., The potential of thin film
1035 nanocomposite membrane in reducing organic fouling in forward osmosis process.
1036 *Desalination* **2014**, *348*, 82-88.

1037 113. Son, M.; Park, H.; Liu, L.; Choi, H.; Kim, J. H.; Choi, H., Thin-film nanocomposite
1038 membrane with CNT positioning in support layer for energy harvesting from saline water.
1039 *Chem. Eng. J.* **2016**, *284*, 68-77.

1040 114. Wu, K.; Liu, Z.; Yu, H.; Kang, G.; Jie, X.; Jin, Y.; Cao, Y., Investigation of internal
1041 concentration polarization reduction in forward osmosis membrane using nano-CaCO₃
1042 particles as sacrificial component. *J. Membr. Sci.* **2015**, *497*, 485-493.

1043 115. Wang, S.; Yi, Z.; Zhao, X.; Zhou, Y.; Gao, C., Aggregation suppressed thin film
1044 nanocomposite (TFN) membranes prepared with an in situ generation of TiO₂ nanoadditives.

1045 RSC Adv. **2017**, 7, (42), 26136-26144.

1046 116. Dong, L.-x.; Huang, X.-c.; Wang, Z.; Yang, Z.; Wang, X.-m.; Tang, C. Y., A thin-film
1047 nanocomposite nanofiltration membrane prepared on a support with in situ embedded zeolite
1048 nanoparticles. *Sep. Purif. Technol.* **2016**, 166, 230-239.

1049 117. Zhou, Z.; Hu, Y.; Boo, C.; Liu, Z.; Li, J.; Deng, L.; An, X., High-Performance Thin-Film
1050 Composite Membrane with an Ultrathin Spray-Coated Carbon Nanotube Interlayer. *Environ.*
1051 *Sci. Technol. Lett.* **2018**, 5, (5), 243-248.

1052 118. Gong, G.; Wang, P.; Zhou, Z.; Hu, Y., New insights into the role of an interlayer for the
1053 fabrication of highly selective and permeable thin-film composite nanofiltration membrane.
1054 *ACS Appl. Mater. Interfaces* **2019**, 11, (7), 7349-7356.

1055 119. Kattula, M.; Ponnuru, K.; Zhu, L.; Jia, W.; Lin, H.; Furlani, E. P., Designing ultrathin
1056 film composite membranes: the impact of a gutter layer. *Sci. Rep.* **2015**, 5, (1), 15016.

1057 120. Liang, C. Z.; Chung, T.-S.; Lai, J.-Y., A review of polymeric composite membranes
1058 for gas separation and energy production. *Prog. Polym. Sci.* **2019**, 97, 101141.

1059 121. Yang, Z.; Zhou, Z. W.; Guo, H.; Yao, Z.; Ma, X. H.; Song, X.; Feng, S. P.; Tang, C.
1060 Y., Tannic Acid/Fe(3+) Nanoscaffold for Interfacial Polymerization: Toward Enhanced
1061 Nanofiltration Performance. *Environ. Sci. Technol.* **2018**, 52, (16), 9341-9349.

1062 122. Zhang, X.; Lv, Y.; Yang, H.-C.; Du, Y.; Xu, Z.-K., Polyphenol Coating as an
1063 Interlayer for Thin-Film Composite Membranes with Enhanced Nanofiltration Performance.
1064 *ACS Appl. Mater. Interfaces* **2016**, 8, (47), 32512-32519.

1065 123. Lai, G. S.; Lau, W. J.; Goh, P. S.; Ismail, A. F.; Tan, Y. H.; Chong, C. Y.;
1066 Krause-Rehberg, R.; Awad, S., Tailor-made thin film nanocomposite membrane incorporated
1067 with graphene oxide using novel interfacial polymerization technique for enhanced water
1068 separation. *Chem. Eng. J.* **2018**, 344, 524-534.

1069 124. Wu, X.; Ding, M.; Xu, H.; Yang, W.; Zhang, K.; Tian, H.; Wang, H.; Xie, Z.,
1070 Scalable Ti₃C₂T_x MXene Interlayered Forward Osmosis Membranes for Enhanced Water
1071 Purification and Organic Solvent Recovery. *ACS Nano* **2020**, 14, (7), 9125-9135.

1072 125. Lee, T. H.; Oh, J. Y.; Hong, S. P.; Lee, J. M.; Roh, S. M.; Kim, S. H.; Park, H. B.,
1073 ZIF-8 particle size effects on reverse osmosis performance of polyamide thin-film
1074 nanocomposite membranes: Importance of particle deposition. *J. Membr. Sci.* **2019**, 570-571,
1075 23-33.

1076 126. Wu, H.; Tang, B.; Wu, P., Optimization, characterization and nanofiltration
1077 properties test of MWNTs/polyester thin film nanocomposite membrane. *J. Membr. Sci.* **2013**,
1078 428, 425-433.

1079 127. Liu, L.; Zhu, G.; Liu, Z.; Gao, C., Effect of MCM-48 nanoparticles on the
1080 performance of thin film nanocomposite membranes for reverse osmosis application.
1081 *Desalination* **2016**, 394, 72-82.

1082 128. de Lannoy, C.-F. o.; Jassby, D.; Gloe, K.; Gordon, A. D.; Wiesner, M. R., Aquatic
1083 biofouling prevention by electrically charged nanocomposite polymer thin film membranes.
1084 *Environ. Sci. Technol.* **2013**, 47, (6), 2760-2768.

1085 129. Yuan, J.; Wu, M.; Wu, H.; Liu, Y.; You, X.; Zhang, R.; Su, Y.; Yang, H.; Shen, J.;
1086 Jiang, Z., Covalent organic framework-modulated interfacial polymerization for ultrathin

1087 desalination membranes. *J. Mater. Chem. A* **2019**, *7*, (44), 25641-25649.

1088 130. Liang, C. Z.; Liu, J. T.; Lai, J. Y.; Chung, T. S., High-performance multiple-layer
1089 PIM composite hollow fiber membranes for gas separation. *J. Membr. Sci.* **2018**, *563*, 93-106.

1090 131. Li, T.; Pan, Y.; Peinemann, K. V.; Lai, Z., Carbon dioxide selective mixed matrix
1091 composite membrane containing ZIF-7 nano-fillers. *J. Membr. Sci.* **2013**, *425-426*, 235-242.

1092 132. Yang, Z.; Wang, F.; Guo, H.; Peng, L. E.; Ma, X.-H.; Song, X.; Wang, Z.; Tang, C. Y.,
1093 Mechanistic insights into the role of polydopamine interlayer towards improved separation
1094 performance of polyamide nanofiltration membranes. *Environ. Sci. Technol.* **2020**, *54*, (18),
1095 11611-11621.

1096 133. Peng, F.; Liu, J.; Li, J., Analysis of the gas transport performance through PDMS/PS
1097 composite membranes using the resistances-in-series model. *J. Membr. Sci.* **2003**, *222*, (1-2),
1098 225-234.

1099 134. Yang, Z.; Wu, Y.; Wang, J.; Cao, B.; Tang, C. Y., In situ reduction of silver by
1100 polydopamine: A novel antimicrobial modification of a thin-film composite polyamide
1101 membrane. *Environ. Sci. Technol.* **2016**, *50*, (17), 9543-9550.

1102 135. Arena, J. T.; McCloskey, B.; Freeman, B. D.; McCutcheon, J. R., Surface
1103 modification of thin film composite membrane support layers with polydopamine: enabling
1104 use of reverse osmosis membranes in pressure retarded osmosis. *J. Membr. Sci.* **2011**, *375*, (1),
1105 55-62.

1106 136. Han, G.; Zhang, S.; Li, X.; Widjojo, N.; Chung, T.-S., Thin film composite forward
1107 osmosis membranes based on polydopamine modified polysulfone substrates with
1108 enhancements in both water flux and salt rejection. *Chem. Eng. Sci.* **2012**, *80*, 219-231.

1109 137. Huang, Y.; Jin, H.; Li, H.; Yu, P.; Luo, Y., Synthesis and characterization of a
1110 polyamide thin film composite membrane based on a polydopamine coated support layer for
1111 forward osmosis. *RSC Adv.* **2015**, *5*, (128), 106113-106121.

1112 138. Ramon, G. Z.; Wong, M. C.; Hoek, E. M., Transport through composite membrane,
1113 part 1: Is there an optimal support membrane? *J. Membr. Sci.* **2012**, *415*, 298-305.

1114 139. Jiang, Z.; Karan, S.; Livingston, A. G., Water transport through ultrathin polyamide
1115 nanofilms used for reverse osmosis. *Adv. Mater.* **2018**, *30*, (15), 1705973.

1116 140. Wu, M.-B.; Lv, Y.; Yang, H.-C.; Liu, L.-F.; Zhang, X.; Xu, Z.-K., Thin film
1117 composite membranes combining carbon nanotube intermediate layer and microfiltration
1118 support for high nanofiltration performances. *J. Membr. Sci.* **2016**, *515*, 238-244.

1119 141. Zhao, W.; Liu, H.; Liu, Y.; Jian, M.; Gao, L.; Wang, H.; Zhang, X., Thin-Film
1120 Nanocomposite Forward-Osmosis Membranes on Hydrophilic Microfiltration Support with
1121 an Intermediate Layer of Graphene Oxide and Multiwall Carbon Nanotube. *ACS Appl. Mater.*
1122 *Interfaces* **2018**, *10*, (40), 34464-34474.

1123 142. Song, X.; Gan, B.; Qi, S.; Guo, H.; Tang, C. Y.; Zhou, Y.; Gao, C., Intrinsic
1124 Nanoscale Structure of Thin Film Composite Polyamide Membranes: Connectivity, Defects,
1125 and Structure-Property Correlation. *Environ. Sci. Technol.* **2020**, *54*, (6), 3559-3569.

1126 143. Lin, L.; Lopez, R.; Ramon, G. Z.; Coronell, O., Investigating the void structure of
1127 the polyamide active layers of thin-film composite membranes. *J. Membr. Sci.* **2016**, *497*,
1128 365-376.

- 1129 144. Chan, W.-F.; Chen, H.-y.; Surapathi, A.; Taylor, M. G.; Shao, X.; Marand, E.;
1130 Johnson, J. K., Zwitterion functionalized carbon nanotube/polyamide nanocomposite
1131 membranes for water desalination. *ACS Nano* **2013**, *7*, (6), 5308-5319.
- 1132 145. Yan, H.; Miao, X.; Xu, J.; Pan, G.; Zhang, Y.; Shi, Y.; Guo, M.; Liu, Y., The porous
1133 structure of the fully-aromatic polyamide film in reverse osmosis membranes. *J. Membr. Sci.*
1134 **2015**, *475*, 504-510.
- 1135 146. Song, X.; Smith, J. W.; Kim, J.; Zaluzec, N. J.; Chen, W.; An, H.; Dennison, J. M.;
1136 Cahill, D. G.; Kulzick, M. A.; Chen, Q., Unraveling the Morphology–Function Relationships
1137 of Polyamide Membranes Using Quantitative Electron Tomography. *ACS Appl. Mater.*
1138 *Interfaces* **2019**, *11*, (8), 8517-8526.
- 1139 147. Song, X.; Gan, B.; Yang, Z.; Tang, C. Y.; Gao, C., Confined nanobubbles shape the
1140 surface roughness structures of thin film composite polyamide desalination membranes. *J.*
1141 *Membr. Sci.* **2019**, *582*, 342-349.
- 1142 148. Peng, L. E.; Yao, Z.; Liu, X.; Deng, B.; Guo, H.; Tang, C. Y., Tailoring Polyamide
1143 Rejection Layer with Aqueous Carbonate Chemistry for Enhanced Membrane Separation:
1144 Mechanistic Insights, Chemistry-Structure-Property Relationship, and Environmental
1145 Implications. *Environ. Sci. Technol.* **2019**, *53*, (16), 9764-9770.
- 1146 149. Peng, L. E.; Yao, Z.; Yang, Z.; Guo, H.; Tang, C. Y., Dissecting the Role of Substrate
1147 on the Morphology and Separation Properties of Thin Film Composite Polyamide
1148 Membranes: Seeing Is Believing. *Environ. Sci. Technol.* **2020**, *54*, (11), 6978-6986.
- 1149 150. Zhang, M.; Jin, W.; Yang, F.; Duke, M.; Dong, Y.; Tang, C. Y., Engineering a
1150 Nanocomposite Interlayer for a Novel Ceramic-Based Forward Osmosis Membrane with
1151 Enhanced Performance. *Environ. Sci. Technol.* **2020**, *54*, (12), 7715-7724.
- 1152 151. Zhu, X.; Cheng, X.; Luo, X.; Liu, Y.; Xu, D.; Tang, X.; Gan, Z.; Yang, L.; Li, G.;
1153 Liang, H., Ultrathin Thin-Film Composite Polyamide Membranes Constructed on
1154 Hydrophilic Poly(vinyl alcohol) Decorated Support Toward Enhanced Nanofiltration
1155 Performance. *Environ. Sci. Technol.* **2020**, *54*, (10), 6365-6374.
- 1156 152. Zhu, X.; Yang, Z.; Gan, Z.; Cheng, X.; Tang, X.; Luo, X.; Xu, D.; Li, G.; Liang, H.,
1157 Toward tailoring nanofiltration performance of thin-film composite membranes: Novel
1158 insights into the role of poly(vinyl alcohol) coating positions. *J. Membr. Sci.* **2020**, *614*,
1159 118526.
- 1160 153. Wu, M.; Yuan, J.; Wu, H.; Su, Y.; Yang, H.; You, X.; Zhang, R.; He, X.; Khan, N. A.;
1161 Kasher, R.; Jiang, Z., Ultrathin nanofiltration membrane with polydopamine-covalent organic
1162 framework interlayer for enhanced permeability and structural stability. *J. Membr. Sci.* **2019**,
1163 *576*, 131-141.
- 1164 154. Culp, T. E.; Shen, Y.-x.; Geitner, M.; Paul, M.; Roy, A.; Behr, M. J.; Rosenberg, S.;
1165 Gu, J.; Kumar, M.; Gomez, E. D., Electron tomography reveals details of the internal
1166 microstructure of desalination membranes. *Proc. Natl. Acad. Sci.* **2018**, *115*, (35), 8694.
- 1167 155. Ghosh, A. K.; Hoek, E. M., Impacts of support membrane structure and chemistry on
1168 polyamide–polysulfone interfacial composite membranes. *J. Membr. Sci.* **2009**, *336*, (1),
1169 140-148.
- 1170 156. Wu, X.; Li, Y.; Cui, X.; Wang, J.; Cao, X.; Zhang, P.; Zheng, L., Adsorption-Assisted

1171 Interfacial Polymerization toward Ultrathin Active Layers for Ultrafast Organic Permeation.
1172 *ACS Appl. Mater. Interfaces* **2018**, *10*, (12), 10445-10453.

1173 157. Zhu, X.; Tang, X.; Luo, X.; Yang, Z.; Cheng, X.; Gan, Z.; Xu, D.; Li, G.; Liang, H.,
1174 Stainless steel mesh supported thin-film composite nanofiltration membranes for enhanced
1175 permeability and regeneration potential. *J. Membr. Sci.* **2021**, *618*, 118738.

1176 158. Zhu, J.; Yuan, S.; Uliana, A.; Hou, J.; Li, J.; Li, X.; Tian, M.; Chen, Y.; Volodin, A.;
1177 der Bruggen, B. V., High-flux thin film composite membranes for nanofiltration mediated by
1178 a rapid co-deposition of polydopamine/piperazine. *J. Membr. Sci.* **2018**, *554*, 97-108.

1179 159. Cheng, C.; Li, P.; Shen, K.; Zhang, T.; Cao, X.; Wang, B.; Wang, X.; Hsiao, B. S.,
1180 Integrated polyamide thin-film nanofibrous composite membrane regulated by functionalized
1181 interlayer for efficient water/isopropanol separation. *J. Membr. Sci.* **2018**, *553*, 70-81.

1182 160. Qiu, W. Z.; Du, Y.; Lv, Y.; Yang, H. C.; Xu, Z. K., Codeposition of catechol–
1183 polyethyleneimine followed by interfacial polymerization for nanofiltration membranes with
1184 enhanced stability. *J. Appl. Polym. Sci.* **2017**, *134*, (42), 45422.

1185 161. Gu, J. E.; Lee, S.; Stafford, C. M.; Lee, J. S.; Choi, W.; Kim, B. Y.; Baek, K. Y.;
1186 Chan, E. P.; Chung, J. Y.; Bang, J.; Lee, J. H., Molecular layer-by-layer assembled thin-film
1187 composite membranes for water desalination. *Adv. Mater.* **2013**, *25*, (34), 4778-82.

1188 162. Liu, B.; Chen, C.; Zhao, P.; Li, T.; Liu, C.; Wang, Q.; Chen, Y.; Crittenden, J.,
1189 Thin-film composite forward osmosis membranes with substrate layer composed of
1190 polysulfone blended with PEG or polysulfone grafted PEG methyl ether methacrylate.
1191 *Frontiers Chem. Sci. Eng.* **2016**, *10*, (4), 562-574.

1192 163. Wang, J.-J.; Yang, H.-C.; Wu, M.-B.; Zhang, X.; Xu, Z.-K., Nanofiltration
1193 membranes with cellulose nanocrystals as an interlayer for unprecedented performance. *J.*
1194 *Mater. Chem. A* **2017**, *5*, (31), 16289-16295.

1195 164. Wei, J.; Liu, X.; Qiu, C.; Wang, R.; Tang, C. Y., Influence of monomer
1196 concentrations on the performance of polyamide-based thin film composite forward osmosis
1197 membranes. *J. Membr. Sci.* **2011**, *381*, (1-2), 110-117.

1198 165. Song, X.; Qi, S.; Tang, C. Y.; Gao, C., Ultra-thin, multi-layered polyamide
1199 membranes: Synthesis and characterization. *J. Membr. Sci.* **2017**, *540*, 10-18.

1200 166. Kang, X.; Liu, X.; Liu, J.; Wen, Y.; Qi, J.; Li, X., Spin-assisted interfacial
1201 polymerization strategy for graphene oxide-polyamide composite nanofiltration membrane
1202 with high performance. *Appl. Surf. Sci.* **2020**, *508*, 145198.

1203 167. Shen, K.; Cheng, C.; Zhang, T.; Wang, X., High performance polyamide composite
1204 nanofiltration membranes via reverse interfacial polymerization with the synergistic
1205 interaction of gelatin interlayer and trimesoyl chloride. *J. Membr. Sci.* **2019**, *588*, 117192.

1206 168. Zhao, D. L.; Chung, T. S., Applications of carbon quantum dots (CQDs) in
1207 membrane technologies: A review. *Water Res* **2018**, *147*, 43-49.

1208 169. Gai, W.; Zhao, D. L.; Chung, T. S., Thin film nanocomposite hollow fiber
1209 membranes comprising Na + -functionalized carbon quantum dots for brackish water
1210 desalination. *Water Res.* **2019**, *154*, 54-61.

1211 170. Lakhotia, S. R.; Mukhopadhyay, M.; Kumari, P., Iron oxide (FeO) nanoparticles
1212 embedded thin-film nanocomposite nanofiltration (NF) membrane for water treatment. *Sep.*

1213 *Purif. Technol.* **2019**, *211*, 98-107.

1214 171. Wang, L.; Fang, M.; Liu, J.; He, J.; Li, J.; Lei, J., Layer-by-Layer Fabrication of
1215 High-Performance Polyamide/ZIF-8 Nanocomposite Membrane for Nanofiltration
1216 Applications. *ACS Appl. Mater. Interfaces* **2015**, *7*, (43), 24082-24093.

1217 172. Wang, Z.; Wang, Z.; Lin, S.; Jin, H.; Gao, S.; Zhu, Y.; Jin, J., Nanoparticle-templated
1218 nanofiltration membranes for ultrahigh performance desalination. *Nat. Commun.* **2018**, *9*, (1),
1219 2004.

1220 173. Lee, T. H.; Park, I.; Oh, J. Y.; Jang, J. K.; Park, H. B., Facile Preparation of
1221 Polyamide Thin-Film Nanocomposite Membranes Using Spray-Assisted Nanofiller
1222 Predeposition. *Ind. Eng. Chem. Res.* **2019**, *58*, (10), 4248-4256.

1223 174. Paseto, L.; Antorán, D.; Coronas, J.; Tólez, C., 110th Anniversary:
1224 Polyamide/Metal–Organic Framework Bilayered Thin Film Composite Membranes for the
1225 Removal of Pharmaceutical Compounds from Water. *Ind. Eng. Chem. Res.* **2019**, *58*, (10),
1226 4222-4230.

1227 175. Wang, Y.; Li, X.; Zhao, S.; Fang, Z.; Ng, D.; Xie, C.; Wang, H.; Xie, Z., Thin-Film
1228 Composite Membrane with Interlayer Decorated Metal–Organic Framework UiO-66 toward
1229 Enhanced Forward Osmosis Performance. *Ind. Eng. Chem. Res.* **2019**, *58*, (1), 195-206.

1230 176. Al Aani, S.; Haroutounian, A.; Wright, C. J.; Hilal, N., Thin Film Nanocomposite
1231 (TFN) membranes modified with polydopamine coated metals/carbon-nanostructures for
1232 desalination applications. *Desalination* **2018**, *427*, 60-74.

1233 177. Shah, A. A.; Cho, Y. H.; Choi, H.-g.; Nam, S.-E.; Kim, J. F.; Kim, Y.; Park, Y.-I.;
1234 Park, H., Facile integration of halloysite nanotubes with bioadhesive as highly permeable
1235 interlayer in forward osmosis membranes. *J. Ind. Eng. Chem.* **2019**, *73*, 276-285.

1236 178. Lai, G. S.; Lau, W. J.; Goh, P. S.; Tan, Y. H.; Ng, B. C.; Ismail, A. F., A novel
1237 interfacial polymerization approach towards synthesis of graphene oxide-incorporated thin
1238 film nanocomposite membrane with improved surface properties. *Arab. J. Chem.* **2019**, *12*,
1239 (1), 75-87.

1240 179. Ingole, P. G.; Choi, W.; Kim, K. H.; Park, C. H.; Choi, W. K.; Lee, H. K., Synthesis,
1241 characterization and surface modification of PES hollow fiber membrane support with
1242 polydopamine and thin film composite for energy generation. *Chem. Eng. J.* **2014**, *243*,
1243 137-146.

1244 180. Ren, Y.; Zhu, J.; Cong, S.; Wang, J.; Van der Bruggen, B.; Liu, J.; Zhang, Y., High
1245 flux thin film nanocomposite membranes based on porous organic polymers for nanofiltration.
1246 *J. Membr. Sci.* **2019**, *585*, 19-28.

1247 181. Ritt, C. L.; Werber, J. R.; Deshmukh, A.; Elimelech, M., Monte Carlo Simulations of
1248 Framework Defects in Layered Two-Dimensional Nanomaterial Desalination Membranes:
1249 Implications for Permeability and Selectivity. *Environ. Sci. Technol.* **2019**, *53*, (11),
1250 6214-6224.

1251 182. Lu, X.; Gabinet, U. R.; Ritt, C.; Feng, X.; Deshmukh, A.; Kawabata, K.; Kaneda, M.;
1252 Hashmi, S. M.; Osuji, C. O.; Elimelech, M., Relating Selectivity and Separation Performance
1253 of Lamellar Two-Dimensional Molybdenum Disulfide (MoS₂) Membranes to Nanosheet
1254 Stacking Behavior. *Environ. Sci. Technol.* **2020**, *54*, (15), 9640-9651.

- 1255 183. Sapkota, B.; Liang, W.; Vahidmohammadi, A.; Karnik, R.; Noy, A.; Wanunu, M.,
1256 High permeability sub-nanometre sieve composite MoS₂ membranes. *Nat. Commun.* **2020**,
1257 *11*, (1), 2747.
- 1258 184. Jian, M.; Qiu, R.; Xia, Y.; Lu, J.; Chen, Y.; Gu, Q.; Liu, R.; Hu, C.; Qu, J.; Wang, H.;
1259 Zhang, X., Ultrathin water-stable metal-organic framework membranes for ion separation. *Sci.*
1260 *Adv.* **2020**, *6*, (23), eaay3998.
- 1261 185. Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B., Mussel-inspired surface
1262 chemistry for multifunctional coatings. *Science* **2007**, *318*, (5849), 426-430.
- 1263 186. Xu, L.; Shan, B.; Gao, C.; Xu, J., Multifunctional thin-film nanocomposite
1264 membranes comprising covalent organic nanosheets with high crystallinity for efficient
1265 reverse osmosis desalination. *J. Membr. Sci.* **2020**, *593*, 117398.
- 1266 187. Zhai, Z.; Jiang, C.; Zhao, N.; Dong, W.; Lan, H.; Wang, M.; Niu, Q. J., Fabrication
1267 of advanced nanofiltration membranes with nanostrand hybrid morphology mediated by
1268 ultrafast Noria–polyethyleneimine codeposition. *J. Mater. Chem. A* **2018**, *6*, (42),
1269 21207-21215.
- 1270 188. Yang, S.; Wang, J.; Fang, L.; Lin, H.; Liu, F.; Tang, C. Y., Electrospayed polyamide
1271 nanofiltration membrane with intercalated structure for controllable structure manipulation
1272 and enhanced separation performance. *J. Membr. Sci.* **2020**, *602*, 117971.
- 1273 189. Tang, C.; Kwon, Y.; Leckie, J., Probing the nano- and micro-scales of reverse
1274 osmosis membranes—A comprehensive characterization of physiochemical properties of
1275 uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential
1276 measurements. *J. Membr. Sci.* **2007**, *287*, (1), 146-156.
- 1277 190. Tang, C. Y.; Kwon, Y.-N.; Leckie, J. O., Effect of membrane chemistry and coating
1278 layer on physiochemical properties of thin film composite polyamide RO and NF membranes:
1279 II. Membrane physiochemical properties and their dependence on polyamide and coating
1280 layers. *Desalination* **2009**, *242*, (1-3), 168-182.
- 1281 191. Tang, C. Y.; Kwon, Y.-N.; Leckie, J. O., Effect of membrane chemistry and coating
1282 layer on physiochemical properties of thin film composite polyamide RO and NF membranes:
1283 I. FTIR and XPS characterization of polyamide and coating layer chemistry. *Desalination*
1284 **2009**, *242*, (1-3), 149-167.
- 1285 192. Greenlee, L. F.; Lawler, D. F.; Freeman, B. D.; Marrot, B.; Moulin, P., Reverse
1286 osmosis desalination: Water sources, technology, and today's challenges. *Water Res.* **2009**, *43*,
1287 (9), 2317-2348.
- 1288 193. Werber, J. R.; Deshmukh, A.; Elimelech, M., The critical need for increased
1289 selectivity, not increased water permeability, for desalination membranes. *Environ. Sci.*
1290 *Technol. Lett.* **2016**, *3*, (4), 112-120.
- 1291 194. Lin, S., Energy Efficiency of Desalination: Fundamental Insights from Intuitive
1292 Interpretation. *Environ. Sci. Technol.* **2019**, *54*, (1), 76-84.
- 1293 195. Cohen-Tanugi, D.; McGovern, R. K.; Dave, S. H.; Lienhard, J. H.; Grossman, J. C.,
1294 Quantifying the potential of ultra-permeable membranes for water desalination. *Energy*
1295 *Environ. Sci.* **2014**, *7*, (3), 1134-1141.
- 1296 196. Semiat, R., Energy Issues in Desalination Processes. *Environ. Sci. Technol.* **2008**, *42*,

1297 (22), 8193-8201.

1298 197. Liu, L.; Xie, X.; Qi, S.; Li, R.; Zhang, X.; Song, X.; Gao, C., Thin film
1299 nanocomposite reverse osmosis membrane incorporated with UiO-66 nanoparticles for
1300 enhanced boron removal. *J. Membr. Sci.* **2019**, *580*, 101-109.

1301 198. Melnyk, L.; Goncharuk, V.; Butnyk, I.; Tsapiuk, E., Boron removal from natural and
1302 wastewaters using combined sorption/membrane process. *Desalination* **2005**, *185*, (1),
1303 147-157.

1304 199. Tang, Y. P.; Luo, L.; Thong, Z.; Chung, T. S., Recent advances in membrane
1305 materials and technologies for boron removal. *J. Membr. Sci.* **2017**, *541*, 434-446.

1306 200. Hu, J.; Pu, Y.; Ueda, M.; Zhang, X.; Wang, L., Charge-aggregate induced (CAI)
1307 reverse osmosis membrane for seawater desalination and boron removal. *J. Membr. Sci.* **2016**,
1308 *520*, 1-7.

1309 201. World Health, O., Boron in drinking-water : background document for development
1310 of WHO guidelines for drinking-water quality. In World Health Organization: Geneva, 2009.

1311 202. Directive, C., On the quality of water intended for human consumption. *Official*
1312 *Journal of the European Communities* **1998**, *330*, 32-54.

1313 203. Wang, S.; Zhou, Y.; Gao, C., Novel high boron removal polyamide reverse osmosis
1314 membranes. *J. Membr. Sci.* **2018**, *554*, 244-252.

1315 204. Koseoglu, H.; Kabay, N.; Yüksel, M.; Sarp, S.; Arar, Ö.; Kitis, M., Boron removal
1316 from seawater using high rejection SWRO membranes — impact of pH, feed concentration,
1317 pressure, and cross-flow velocity. *Desalination* **2008**, *227*, (1-3), 253-263.

1318 205. Hua, G.; Reckhow, D. A.; Kim, J., Effect of Bromide and Iodide Ions on the
1319 Formation and Speciation of Disinfection Byproducts during Chlorination. *Environ. Sci.*
1320 *Technol.* **2006**, *40*, (9), 3050-3056.

1321 206. Dorji, P.; Choi, J.; Kim, D. I.; Phuntsho, S.; Hong, S.; Shon, H. K., Membrane
1322 capacitive deionisation as an alternative to the 2nd pass for seawater reverse osmosis
1323 desalination plant for bromide removal. *Desalination* **2018**, *433*, 113-119.

1324 207. Listiarini, K.; Tor, J. T.; Sun, D. D.; Leckie, J. O., Hybrid coagulation–nanofiltration
1325 membrane for removal of bromate and humic acid in water. *J. Membr. Sci.* **2010**, *365*, (1),
1326 154-159.

1327 208. Kampioti, A. A.; Stephanou, E. G., The impact of bromide on the formation of
1328 neutral and acidic disinfection by-products (DBPs) in Mediterranean chlorinated drinking
1329 water. *Water Res.* **2002**, *36*, (10), 2596-2606.

1330 209. Dorji, P.; Kim, D. I.; Hong, S.; Phuntsho, S.; Shon, H. K., Pilot-scale membrane
1331 capacitive deionisation for effective bromide removal and high water recovery in seawater
1332 desalination. *Desalination* **2020**, *479*, 114309.

1333 210. Shaffer, D. L.; Yip, N. Y.; Gilron, J.; Elimelech, M., Seawater desalination for
1334 agriculture by integrated forward and reverse osmosis: Improved product water quality for
1335 potentially less energy. *J. Membr. Sci.* **2012**, *415-416*, 1-8.

1336 211. Guo, H.; Peng, L. E.; Yao, Z.; Yang, Z.; Ma, X.; Tang, C. Y., Non-Polyamide Based
1337 Nanofiltration Membranes Using Green Metal–Organic Coordination Complexes:
1338 Implications for the Removal of Trace Organic Contaminants. *Environ. Sci. Technol.* **2019**, *53*,

1339 (5), 2688-2694.

1340 212. Radjenović, J.; Petrović, M.; Ventura, F.; Barceló, D., Rejection of pharmaceuticals
1341 in nanofiltration and reverse osmosis membrane drinking water treatment. *Water Res.* **2008**,
1342 *42*, (14), 3601-3610.

1343 213. Taheran, M.; Brar, S. K.; Verma, M.; Surampalli, R. Y.; Zhang, T. C.; Valero, J. R.,
1344 Membrane processes for removal of pharmaceutically active compounds (PhACs) from water
1345 and wastewaters. *Sci. Total Environ.* **2016**, *547*, 60-77.

1346 214. Mi, B.; Eaton, C. L.; Kim, J.-H.; Colvin, C. K.; Lozier, J. C.; Mariñas, B. J.,
1347 Removal of biological and non-biological viral surrogates by spiral-wound reverse osmosis
1348 membrane elements with intact and compromised integrity. *Water Res.* **2004**, *38*, (18),
1349 3821-3832.

1350 215. Hornstra, L. M.; Rodrigues Da Silva, T.; Blankert, B.; Heijnen, L.; Beerendonk, E.;
1351 Cornelissen, E. R.; Medema, G., Monitoring the integrity of reverse osmosis membranes
1352 using novel indigenous freshwater viruses and bacteriophages. *Environ. Sci. Water Res.*
1353 *Technol.* **2019**, *5*, (9), 1535-1544.

1354 216. Harisha, R. S.; Hosamani, K. M.; Keri, R. S.; Nataraj, S. K.; Aminabhavi, T. M.,
1355 Arsenic removal from drinking water using thin film composite nanofiltration membrane.
1356 *Desalination* **2010**, *252*, (1-3), 75-80.

1357 217. Fu, F.; Wang, Q., Removal of heavy metal ions from wastewaters: A review. *J.*
1358 *Environ. Manage* **2011**, *92*, (3), 407-418.

1359 218. Boo, C.; Wang, Y.; Zucker, I.; Choo, Y.; Osuji, C. O.; Elimelech, M., High
1360 Performance Nanofiltration Membrane for Effective Removal of Perfluoroalkyl Substances at
1361 High Water Recovery. *Environ. Sci. Technol.* **2018**, *52*, (13), 7279-7288.

1362 219. Steinle-Darling, E.; Reinhard, M., Nanofiltration for Trace Organic Contaminant
1363 Removal: Structure, Solution, and Membrane Fouling Effects on the Rejection of
1364 Perfluorochemicals. *Environ. Sci. Technol.* **2008**, *42*, (14), 5292-5297.

1365 220. Kimura, K.; Amy, G.; Drewes, J. E.; Heberer, T.; Kim, T.-U.; Watanabe, Y.,
1366 Rejection of organic micropollutants (disinfection by-products, endocrine disrupting
1367 compounds, and pharmaceutically active compounds) by NF/RO membranes. *J. Membr. Sci.*
1368 **2003**, *227*, (1-2), 113-121.

1369 221. Löwenberg, J.; Baum, J. A.; Zimmermann, Y.-S.; Groot, C.; van den Broek, W.;
1370 Wintgens, T., Comparison of pre-treatment technologies towards improving reverse osmosis
1371 desalination of cooling tower blow down. *Desalination* **2015**, *357*, 140-149.

1372 222. Al-Zoubi, H.; Rieger, A.; Steinberger, P.; Pelz, W.; Haseneder, R.; Härtel, G.,
1373 Optimization study for treatment of acid mine drainage using membrane technology. *Sep. Sci.*
1374 *Technol.* **2010**, *45*, (14), 2004-2016.

1375 223. Ricci, B. C.; Ferreira, C. D.; Aguiar, A. O.; Amaral, M. C. S., Integration of
1376 nanofiltration and reverse osmosis for metal separation and sulfuric acid recovery from gold
1377 mining effluent. *Sep. Purif. Technol.* **2015**, *154*, 11-21.

1378 224. Pino, L.; Vargas, C.; Schwarz, A.; Borquez, R., Influence of operating conditions on
1379 the removal of metals and sulfate from copper acid mine drainage by nanofiltration. *Chem.*
1380 *Eng. J.* **2018**, *345*, 114-125.

- 1381 225. Li, X.; Mo, Y.; Qing, W.; Shao, S.; Tang, C. Y.; Li, J., Membrane-based technologies
1382 for lithium recovery from water lithium resources: A review. *J. Membr. Sci.* **2019**, *591*,
1383 117317.
- 1384 226. Gwak, G.; Kim, D. I.; Hong, S., New industrial application of forward osmosis (FO):
1385 Precious metal recovery from printed circuit board (PCB) plant wastewater. *J. Membr. Sci.*
1386 **2018**, *552*, 234-242.
- 1387 227. Daraei, P.; Madaeni, S. S.; Salehi, E.; Ghaemi, N.; Ghari, H. S.; Khadivi, M. A.;
1388 Rostami, E., Novel thin film composite membrane fabricated by mixed matrix
1389 nanoclay/chitosan on PVDF microfiltration support: Preparation, characterization and
1390 performance in dye removal. *J. Membr. Sci.* **2013**, *436*, 97-108.
- 1391 228. Ormanci-Acar, T.; Celebi, F.; Keskin, B.; Mutlu-Salmanlı, O.; Agtas, M.; Turken, T.;
1392 Tufani, A.; Imer, D. Y.; Ince, G. O.; Demir, T. U.; Menciloglu, Y. Z.; Unal, S.; Koyuncu, I.,
1393 Fabrication and characterization of temperature and pH resistant thin film nanocomposite
1394 membranes embedded with halloysite nanotubes for dye rejection. *Desalination* **2018**, *429*,
1395 20-32.
- 1396 229. Li, M.; Yao, Y.; Zhang, W.; Zheng, J.; Zhang, X.; Wang, L., Fractionation and
1397 Concentration of High-Salinity Textile Wastewater using an Ultra-Permeable Sulfonated
1398 Thin-film Composite. *Environ. Sci. Technol.* **2017**, *51*, (16), 9252-9260.
- 1399 230. Fang, S.-Y.; Zhang, P.; Gong, J.-L.; Tang, L.; Zeng, G.-M.; Song, B.; Cao, W.-C.; Li,
1400 J.; Ye, J., Construction of highly water-stable metal-organic framework UiO-66 thin-film
1401 composite membrane for dyes and antibiotics separation. *Chem. Eng. J.* **2020**, *385*, 123400.
- 1402 231. Peng, L. E.; Yao, Z.; Chen, J.; Guo, H.; Tang, C. Y., Highly selective separation and
1403 resource recovery using forward osmosis membrane assembled by polyphenol network. *J.*
1404 *Membr. Sci.* **2020**, *611*, 118305.
- 1405 232. Niewersch, C.; Bloch, A. B.; Yüce, S.; Melin, T.; Wessling, M., Nanofiltration for
1406 the recovery of phosphorus—Development of a mass transport model. *Desalination* **2014**,
1407 *346*, 70-78.
- 1408 233. Xie, M.; Nghiem, L. D.; Price, W. E.; Elimelech, M., Toward resource recovery from
1409 wastewater: extraction of phosphorus from digested sludge using a hybrid forward osmosis–
1410 membrane distillation process. *Environ. Sci. Technol. Lett.* **2014**, *1*, (2), 191-195.
- 1411 234. Li, X.; Zhang, C.; Zhang, S.; Li, J.; He, B.; Cui, Z., Preparation and characterization
1412 of positively charged polyamide composite nanofiltration hollow fiber membrane for lithium
1413 and magnesium separation. *Desalination* **2015**, *369*, 26-36.
- 1414 235. Hancock, N. T.; Black, N. D.; Cath, T. Y., A comparative life cycle assessment of
1415 hybrid osmotic dilution desalination and established seawater desalination and wastewater
1416 reclamation processes. *Water Res.* **2012**, *46*, (4), 1145-1154.
- 1417 236. Stevens, D. M.; Shu, J. Y.; Reichert, M.; Roy, A., Next-Generation Nanoporous
1418 Materials: Progress and Prospects for Reverse Osmosis and Nanofiltration. *Ind. Eng. Chem.*
1419 *Res.* **2017**, *56*, (38), 10526-10551.
- 1420 237. Shultz, S.; Bass, M.; Semiat, R.; Freger, V., Modification of polyamide membranes
1421 by hydrophobic molecular plugs for improved boron rejection. *J. Membr. Sci.* **2018**, *546*,
1422 165-172.

- 1423 238. Le Roux, J.; Gallard, H.; Croué J.-P., Formation of NDMA and Halogenated DBPs
1424 by Chloramination of Tertiary Amines: The Influence of Bromide Ion. *Environ. Sci. Technol.*
1425 **2012**, *46*, (3), 1581-1589.
- 1426 239. Ged, E. C.; Boyer, T. H., Effect of seawater intrusion on formation of
1427 bromine-containing trihalomethanes and haloacetic acids during chlorination. *Desalination*
1428 **2014**, *345*, 85-93.
- 1429 240. Wang, J.; Hao, Z.; Shi, F.; Yin, Y.; Cao, D.; Yao, Z.; Liu, J., Characterization of
1430 Brominated Disinfection Byproducts Formed During the Chlorination of Aquaculture
1431 Seawater. *Environ. Sci. Technol.* **2018**, *52*, (10), 5662-5670.
- 1432 241. Kim, D.; Amy, G. L.; Karanfil, T., Disinfection by-product formation during
1433 seawater desalination: A review. *Water Res.* **2015**, *81*, 343-355.
- 1434 242. Warsinger, D. M.; Chakraborty, S.; Tow, E. W.; Plumlee, M. H.; Bellona, C.;
1435 Loutatidou, S.; Karimi, L.; Mikelonis, A. M.; Achilli, A.; Ghassemi, A.; Padhye, L. P.; Snyder,
1436 S. A.; Curcio, S.; Vecitis, C. D.; Arafat, H. A.; Lienhard, J. H., A review of polymeric
1437 membranes and processes for potable water reuse. *Prog. Polym. Sci.* **2018**, *81*, 209-237.
- 1438 243. Chung, T.-S.; Zhao, D.; Gao, J.; Lu, K.; Wan, C.; Weber, M.; Maletzko, C.,
1439 Emerging R&D on membranes and systems for water reuse and desalination. *Chin. J. Chem.*
1440 *Eng.* **2019**, *27*, (7), 1578-1585.
- 1441 244. Pisarenko, A. N.; Stanford, B. D.; Yan, D.; Gerrity, D.; Snyder, S. A., Effects of
1442 ozone and ozone/peroxide on trace organic contaminants and NDMA in drinking water and
1443 water reuse applications. *Water Res.* **2012**, *46*, (2), 316-326.
- 1444 245. Fujioka, T.; Khan, S. J.; Poussade, Y.; Drewes, J. E.; Nghiem, L. D., N-nitrosamine
1445 removal by reverse osmosis for indirect potable water reuse – A critical review based on
1446 observations from laboratory-, pilot- and full-scale studies. *Sep. Purif. Technol.* **2012**, *98*,
1447 503-515.
- 1448 246. McCurry, D. L.; Ishida, K. P.; Oelker, G. L.; Mitch, W. A., Reverse Osmosis Shifts
1449 Chloramine Speciation Causing Re-Formation of NDMA during Potable Reuse of
1450 Wastewater. *Environ. Sci. Technol.* **2017**, *51*, (15), 8589-8596.
- 1451 247. Guo, H.; Deng, Y.; Yao, Z.; Yang, Z.; Wang, J.; Lin, C.; Zhang, T.; Zhu, B.; Tang, C.
1452 Y., A highly selective surface coating for enhanced membrane rejection of endocrine
1453 disrupting compounds: Mechanistic insights and implications. *Water Res.* **2017**, *121*,
1454 197-203.
- 1455 248. Pype, M.-L.; Lawrence, M. G.; Keller, J.; Gernjak, W., Reverse osmosis integrity
1456 monitoring in water reuse: The challenge to verify virus removal – A review. *Water Res.* **2016**,
1457 *98*, 384-395.
- 1458 249. Yoon, S.-H., Potential and limitation of fluorescence-based membrane integrity
1459 monitoring (FMIM) for reverse osmosis membranes. *Water Res.* **2019**, *154*, 287-297.
- 1460 250. Pype, M.-L.; Donose, B. C.; Martí L.; Patureau, D.; Wery, N.; Gernjak, W., Virus
1461 removal and integrity in aged RO membranes. *Water Res.* **2016**, *90*, 167-175.
- 1462 251. Van der Bruggen, B.; Everaert, K.; Wilms, D.; Vandecasteele, C., Application of
1463 nanofiltration for removal of pesticides, nitrate and hardness from ground water: rejection
1464 properties and economic evaluation. *J. Membr. Sci.* **2001**, *193*, (2), 239-248.

- 1465 252. Fang, W.; Shi, L.; Wang, R., Mixed polyamide-based composite nanofiltration
1466 hollow fiber membranes with improved low-pressure water softening capability. *J. Membr.*
1467 *Sci.* **2014**, *468*, 52-61.
- 1468 253. Zarei, F.; Moattari, R. M.; Rajabzadeh, S.; Bagheri, M.; Taghizadeh, A.; Mohammadi,
1469 T.; Matsuyama, H., Preparation of thin film composite nano-filtration membranes for
1470 brackish water softening based on the reaction between functionalized UF membranes and
1471 polyethyleneimine. *J. Membr. Sci.* **2019**, *588*, 117207.
- 1472 254. Lv, J.; Wang, K. Y.; Chung, T.-S., Investigation of amphoteric polybenzimidazole
1473 (PBI) nanofiltration hollow fiber membrane for both cation and anions removal. *J. Membr.*
1474 *Sci.* **2008**, *310*, (1), 557-566.
- 1475 255. Shen, J.; Schäfer, A., Removal of fluoride and uranium by nanofiltration and reverse
1476 osmosis: A review. *Chemosphere* **2014**, *117*, 679-691.
- 1477 256. Tang, C. Y.; Fu, Q. S.; Robertson, A. P.; Criddle, C. S.; Leckie, J. O., Use of Reverse
1478 Osmosis Membranes to Remove Perfluorooctane Sulfonate (PFOS) from Semiconductor
1479 Wastewater. *Environ. Sci. Technol.* **2006**, *40*, (23), 7343-7349.
- 1480 257. Tang, C. Y.; Fu, Q. S.; Criddle, C. S.; Leckie, J. O., Effect of Flux (Transmembrane
1481 Pressure) and Membrane Properties on Fouling and Rejection of Reverse Osmosis and
1482 Nanofiltration Membranes Treating Perfluorooctane Sulfonate Containing Wastewater.
1483 *Environ. Sci. Technol.* **2007**, *41*, (6), 2008-2014.
- 1484 258. Zhao, C.; Zhang, J.; He, G.; Wang, T.; Hou, D.; Luan, Z., Perfluorooctane sulfonate
1485 removal by nanofiltration membrane the role of calcium ions. *Chem. Eng. J.* **2013**, *233*,
1486 224-232.
- 1487 259. Khanzada, N. K.; Farid, M. U.; Kharraz, J. A.; Choi, J.; Tang, C. Y.; Nghiem, L. D.;
1488 Jang, A.; An, A. K., Removal of organic micropollutants using advanced membrane-based
1489 water and wastewater treatment: A review. *J. Membr. Sci.* **2020**, *598*, 117672.
- 1490 260. Yu, X.; Yang, H.; Lei, H.; Shapiro, A., Experimental evaluation on concentrating
1491 cooling tower blowdown water by direct contact membrane distillation. *Desalination* **2013**,
1492 *323*, 134-141.
- 1493 261. Zhang, J.; Zeng, H.; Ye, C.; Chen, L.; Yan, X., Pilot test of UF pretreatment prior to
1494 RO for cooling tower blowdown reuse of power plant. *Desalination* **2008**, *222*, (1), 9-16.
- 1495 262. Boricha, A. G.; Murthy, Z. V. P., Preparation, characterization and performance of
1496 nanofiltration membranes for the treatment of electroplating industry effluent. *Sep. Purif.*
1497 *Technol.* **2009**, *65*, (3), 282-289.
- 1498 263. Huang, L.; Bui, N.-N.; Meyering, M. T.; Hamlin, T. J.; McCutcheon, J. R., Novel
1499 hydrophilic nylon 6,6 microfiltration membrane supported thin film composite membranes
1500 for engineered osmosis. *J. Membr. Sci.* **2013**, *437*, 141-149.
- 1501 264. Zhu, W.-P.; Gao, J.; Sun, S.-P.; Zhang, S.; Chung, T.-S., Poly(amidoamine)
1502 dendrimer (PAMAM) grafted on thin film composite (TFC) nanofiltration (NF) hollow fiber
1503 membranes for heavy metal removal. *J. Membr. Sci.* **2015**, *487*, 117-126.
- 1504 265. Hosseini, S. S.; Nazif, A.; Alaei Shahmirzadi, M. A.; Ortiz, I., Fabrication, tuning
1505 and optimization of poly (acrylonitrile) nanofiltration membranes for effective nickel and
1506 chromium removal from electroplating wastewater. *Sep. Purif. Technol.* **2017**, *187*, 46-59.

- 1507 266. Juholin, P.; Kääriäinen, M.-L.; Riihimäki, M.; Sliz, R.; Aguirre, J. L.; Piriälä, M.;
1508 Fabritius, T.; Cameron, D.; Keiski, R. L., Comparison of ALD coated nanofiltration
1509 membranes to unmodified commercial membranes in mine wastewater treatment. *Sep. Purif.*
1510 *Technol.* **2018**, *192*, 69-77.
- 1511 267. Guo, Y.; Ying, Y.; Mao, Y.; Peng, X.; Chen, B., Polystyrene Sulfonate Threaded
1512 through a Metal-Organic Framework Membrane for Fast and Selective Lithium-Ion
1513 Separation. *Angew. Chem.* **2016**, *55*, (48), 15120-15124.
- 1514 268. Xie, M.; Shon, H. K.; Gray, S. R.; Elimelech, M., Membrane-based processes for
1515 wastewater nutrient recovery: Technology, challenges, and future direction. *Water Res.* **2016**,
1516 *89*, 210-221.
- 1517 269. Bai, L.; Liu, Y.; Ding, A.; Ren, N.; Li, G.; Liang, H., Fabrication and
1518 characterization of thin-film composite (TFC) nanofiltration membranes incorporated with
1519 cellulose nanocrystals (CNCs) for enhanced desalination performance and dye removal.
1520 *Chem. Eng. J.* **2019**, *358*, 1519-1528.
- 1521 270. Liu, M.; He, Q.; Zhang, K.; Guo, Z.; Lü, Z.; Yu, S.; Gao, C., Carbodiimide-assisted
1522 zwitterionic modification of poly(piperazine amide) thin-film composite membrane for
1523 enhanced separation and anti-depositing performances to cationic/anionic dye aqueous
1524 solutions. *J. Hazard. Mater.* **2020**, *396*, 122582.
- 1525 271. Chowdhury, M. R.; Steffes, J.; Huey, B. D.; McCutcheon, J. R. J. S., 3D printed
1526 polyamide membranes for desalination. *Science* **2018**, *361*, (6403), 682-686.
- 1527 272. Shi, B.; Marchetti, P.; Peshev, D.; Zhang, S.; Livingston, A. G., Will ultra-high
1528 permeance membranes lead to ultra-efficient processes? Challenges for molecular separations
1529 in liquid systems. *J. Membr. Sci.* **2017**, *525*, 35-47.
- 1530 273. Tang, C. Y.; Chong, T.; Fane, A. G., Colloidal interactions and fouling of NF and RO
1531 membranes: a review. *Adv. Colloid Interface Sci.* **2011**, *164*, (1-2), 126-143.
- 1532 274. Fane, A. G.; Tang, C. Y.; Wang, R., Membrane Technology for Water: Microfiltration,
1533 Ultrafiltration, Nanofiltration, and Reverse Osmosis. In *Treatise Water Sci.*, Wilderer, P., Ed.
1534 Elsevier: Oxford, 2011; pp 301-335.
- 1535 275. Park, H. B.; Kamcev, J.; Robeson, L. M.; Elimelech, M.; Freeman, B. D.,
1536 Maximizing the right stuff: The trade-off between membrane permeability and selectivity.
1537 *Science* **2017**, *356*, (6343), eaab0530.
- 1538 276. Epsztein, R.; Duchanois, R. M.; Ritt, C. L.; Noy, A.; Elimelech, M., Towards
1539 single-species selectivity of membranes with subnanometre pores. *Nat. Nanotechnol.* **2020**,
1540 *15*, (6), 426-436.
- 1541 277. Yang, Z.; Huang, X.; Wang, J.; Tang, C.; Engineering, Novel
1542 polyethyleneimine/TMC-based nanofiltration membrane prepared on a polydopamine coated
1543 substrate. *Frontiers Chem. Sci. Eng.* **2018**, *12*, (2), 273-282.
- 1544 278. Shang, W.; Sun, F.; Jia, W.; Guo, J.; Yin, S.; Wong, P. W.; An, A. K.,
1545 High-performance nanofiltration membrane structured with enhanced stripe
1546 nano-morphology. *J. Membr. Sci.* **2020**, *600*, 117852.
- 1547 279. Schäfer, A.; Nghiem, L.; Waite, T., Removal of the natural hormone estrone from
1548 aqueous solutions using nanofiltration and reverse osmosis. *Environ. Sci. Technol.* **2003**, *37*,

1549 (1), 182-188.

1550 280. Kimura, K.; Toshima, S.; Amy, G.; Watanabe, Y., Rejection of neutral endocrine
1551 disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO
1552 membranes. *J. Membr. Sci.* **2004**, *245*, (1-2), 71-78.

1553 281. Ji, W.; Xiao, L.; Ling, Y.; Ching, C.; Matsumoto, M.; Bisbey, R. P.; Helbling, D. E.;
1554 Dichtel, W. R., Removal of GenX and Perfluorinated Alkyl Substances from Water by
1555 Amine-Functionalized Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140*, (40),
1556 12677-12681.

1557 282. Cath, T.; Childress, A.; Elimelech, M., Forward osmosis: Principles, applications,
1558 and recent developments. *J. Membr. Sci.* **2006**, *281*, (1-2), 70-87.

1559 283. Zhao, S.; Zou, L.; Tang, C. Y.; Mulcahy, D., Recent developments in forward
1560 osmosis: Opportunities and challenges. *J. Membr. Sci.* **2012**, *396*, 1-21.

1561 284. Coronell, O.; Mariñas, B. J.; Zhang, X.; Cahill, D. G., Quantification of Functional
1562 Groups and Modeling of Their Ionization Behavior in the Active Layer of FT30 Reverse
1563 Osmosis Membrane. *Environ. Sci. Technol.* **2008**, *42*, (14), 5260-5266.

1564 285. Coronell, O.; González, M. I.; Mariñas, B. J.; Cahill, D. G., Ionization Behavior,
1565 Stoichiometry of Association, and Accessibility of Functional Groups in the Active Layers of
1566 Reverse Osmosis and Nanofiltration Membranes. *Environ. Sci. Technol.* **2010**, *44*, (17),
1567 6808-6814.

1568 286. Stolov, M.; Freger, V., Degradation of Polyamide Membranes Exposed to Chlorine:
1569 An Impedance Spectroscopy Study. *Environ. Sci. Technol.* **2019**, *53*, (5), 2618-2625.

1570 287. Stolov, M.; Freger, V., Membrane Charge Weakly Affects Ion Transport in Reverse
1571 Osmosis. *Environ. Sci. Technol. Lett.* **2020**, *7*, (6), 440-445.

1572 288. Kim, S. H.; Kwak, S.-Y.; Suzuki, T., Positron annihilation spectroscopic evidence to
1573 demonstrate the flux-enhancement mechanism in morphology-controlled thin-film-composite
1574 (TFC) membrane. *Environ. Sci. Technol.* **2005**, *39*, (6), 1764-1770.

1575 289. Gan, B.; Qi, S.; Song, X.; Yang, Z.; Tang, C. Y.; Cao, X.; Zhou, Y.; Gao, C.,
1576 Ultrathin polyamide nanofilm with an asymmetrical structure: A novel strategy to boost the
1577 permeance of reverse osmosis membranes. *J. Membr. Sci.* **2020**, *612*, 118402.

1578 290. Pacheco, F.; Sougrat, R.; Reinhard, M.; Leckie, J. O.; Pinnau, I., 3D visualization of
1579 the internal nanostructure of polyamide thin films in RO membranes. *J. Membr. Sci.* **2016**,
1580 *501*, 33-44.

1581 291. Tang, C. Y.; Yang, Z., Chapter 8 - Transmission Electron Microscopy (TEM). In
1582 *Membrane Characterization*, Hilal, N.; Ismail, A. F.; Matsuura, T.; Oatley-Radcliffe, D., Eds.
1583 Elsevier: 2017; pp 145-159.

1584 292. Reis, R.; Dumeé, L. F.; He, L.; She, F.; Orbell, J. D.; Winther-Jensen, B.; Duke, M.
1585 C., Amine Enrichment of Thin-Film Composite Membranes via Low Pressure Plasma
1586 Polymerization for Antimicrobial Adhesion. *ACS Appl. Mater. Interfaces* **2015**, *7*, (27),
1587 14644-14653.

1588 293. Kłosowski, M. M.; McGilvery, C. M.; Li, Y.; Abellan, P.; Ramasse, Q.; Cabral, J. T.;
1589 Livingston, A. G.; Porter, A. E., Micro-to nano-scale characterisation of polyamide structures
1590 of the SW30HR RO membrane using advanced electron microscopy and stain tracers. *J.*

1591 *Membr. Sci.* **2016**, *520*, 465-476.
1592 294. Liu, J.; Huang, T.; Ji, R.; Wang, Z.; Tang, C. Y.; Leckie, J. O., Stochastic Collision–
1593 Attachment-Based Monte Carlo Simulation of Colloidal Fouling: Transition from Foulant–
1594 Clean-Membrane Interaction to Foulant–Fouled-Membrane Interaction. *Environ. Sci. Technol.*
1595 **2020**, *54*, (19), 12703-12712.
1596 295. Lee, S.; Boo, C.; Elimelech, M.; Hong, S., Comparison of fouling behavior in
1597 forward osmosis (FO) and reverse osmosis (RO). *J. Membr. Sci.* **2010**, *365*, (1), 34-39.
1598 296. Mo, Y.; Tiraferri, A.; Yip, N. Y.; Adout, A.; Huang, X.; Elimelech, M., Improved
1599 antifouling properties of polyamide nanofiltration membranes by reducing the density of
1600 surface carboxyl groups. *Environ. Sci. Technol.* **2012**, *46*, (24), 13253-13261.
1601 297. Hoek, E. M.; Elimelech, M., Cake-enhanced concentration polarization: a new
1602 fouling mechanism for salt-rejecting membranes. *Environ. Sci. Technol.* **2003**, *37*, (24),
1603 5581-5588.
1604