SYNTHESIS AND CHARACTERIZATION OF THIN FILM NANOCOMPOSITE REVERSE OSMOSIS MEMBRANE FOR SALT AND BORON REMOVAL

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To my beloved parents and siblings

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ABSTRACT

In this study, the effects of organic solvents, heat treatment methods, post-interfacial polymerization (IP) rinsing (prior to membrane heat treatment) and additives on the properties of thin film composite (TFC) membranes were investigated prior to the fabrication of thin film nanocomposite (TFN) membranes incorporated with inorganic nanomaterials. It was found that the preservation of substrate pore structures and the removal of excess monomers and organic solvent from the membrane surface are imperative to fabricate reproducible TFC membranes with consistently high water flux and salt rejection. The main findings from investigating the IP parameters are i) keeping the substrate at minimal heat exposure could prevent substrate pore collapse that potentially reduces the membrane water permeability, ii) rinsing membranes with pure n-hexane after IP resulted in membranes having higher pure water flux (PWF) without significantly decreasing solute rejection, iii) the membrane performances became practically the same after post-IP rinsing, regardless of the solvent used in the IP reaction and iv) membranes fabricated using triethylamine-camphorsulfonic acid-sodium dodecyl sulfate (TEA-CSA-SDS) additives exhibited higher PWF and salt rejection than the membranes fabricated in the absence of the additive. For the TFN membranes, it was found that nanomaterial structures (i.e., sizes and shapes) affect the separation performance of the resultant TFN membranes. Noticeably, titanium-based nanomaterial in spindle-like nanoporous structure (f-nTiO_2) yielded membrane of better filtration performances than its tubular structure – functionalized titanate nanotube (f-TNT). Compared to TFN-f-TNT membrane, TFN-f-nTiO_2 membrane possessed greater water flux (4.26 *vs.* 3.36 L/m^2·h·bar), NaCl (98.04 *vs.* 97.28%) and boron rejection (54.82 *vs.* 48.86%). Ultimately, the incorporation of nanomaterial into membrane selective layer was found to improve membrane water flux at the expense of NaCl and boron rejection in comparison to the TFC membranes. Surface coating of TFN membranes with polyvinyl alcohol (PVA) was found to be effective to recover membrane solute rejection, with slight reduction in water flux. The synergic effect of nanomaterial incorporation and PVA coating resulted in improved membrane water flux without trading off its solute rejection.

ABSTRAK

Dalam kajian ini, kesan-kesan pelarut organik, kaedah rawatan haba, pembilasan pasca pempolimeran antara muka (IP) (sebelum rawatan haba) dan bahan tambahan terhadap sifat membran komposit filem nipis (TFC) telah dikaji sebelum penghasilan membran nanokomposit filem nipis (TFN) yang mengandungi bahan nano bukan organik. Ia didapati bahawa pemeliharaan struktur liang substrat dan pengeluaran monomer dan pelarut organik yang berlebihan daripada permukaan membran adalah penting bagi menghasilkan membran TFC yang boleh direproduksi dan mempunyai kebolehtelapan air dan penolakan garam yang tinggi dan konsisten. Antara penemuan utama dalam kajian parameter IP ialah i) pendedahan substrat pada rawatan haba yang minimum boleh mengelakkan keruntuhan liang substrat yang berpotensi mengurangkan kebolehtelapan air membran, ii) pembilasan membran dengan n-heksana tulen selepas IP menghasilkan membran yang mempunyai kebolehtelapan air tulen (PWF) yang lebih tinggi tanpa mengurangkan penolakan pelarut, iii) prestasi membran menjadi sama selepas pembilasan pasca IP, tidak kira jenis pelarut yang digunakan semasa reaksi IP dan iv) membran yang dihasilkan menggunakan bahan tambahan triethylamine-camphorsulfonic acid-sodium dodecyl sulfate (TEA-CSA-SDS) mempunyai PWF dan penolakan garam yang lebih tinggi berbanding membran yang dihasilkan tanpa bahan tambahan. Bagi membran TFN, didapati bahawa struktur nanomaterial (i.e., saiz dan bentuk) mempengaruhi prestasi membran. Secara ketaranya, representasi bahan nano berasas titanium dalam bentuk gelendong berliang (f-nTiO_2) menghasilkan membran yang berprestasi lebih baik daripada representasinya dalam bentuk tiub (f-TNT). Berbanding dengan membran TFN-f-TNT, membran TFN-f-nTiO_2 mempunyai kebolehtelapan air (4.26 *vs.* 3.36 L/m^2·h·bar), penolakan NaCl (98.04 *vs.* 97.28%) dan boron (54.82 *vs.* 48.86%) yang lebih tinggi. Akhirnya, penggabungan bahan nano ke dalam lapisan selaput membran dapat meningkatkan kebolehtelapan air membran tetapi menjejaskan penolakan NaCl dan boron. Penyalutan permukaan membran TFN dengan alkohol polivinil (PVA) didapati berkesan untuk memulihkan penolakan larut membran, dengan sedikit pengurangan pada kebolehtelapan air. Kesan sinergi daripada penggabungan bahan nano dan penyalutan dengan PVA dapat meningkatkan kebolehtelapan air membran tanpa menjejaskan penolakan larut.

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LIST OF ABBREVIATIONS

AAPTS	-	1-(2-Amino-ethyl)-3-aminopropyl trimethoxysilane
AFM	-	Atomic force microscopy
ATR	-	Attenuated-total-reflectance
BET	-	Brunauer-Emmett-Teller
BWRO	-	Brackish water reverse osmosis
CA	-	Cellulose acetate
$CaCl_2$	-	Calcium chloride
CDBR	-	Concurrent desalination and boron removal
CFIC	-	5-chloroformyloxyisophthaloyl chloride
CNT	-	Carbon nanotube
CSA	-	Camphorsulfonic acid
ED	-	Electrodialysis
EDBSA	-	4,4'-(1,2-ethanediyldiimino)bis(benzenesulfonic acid)
EDR	-	Electrodialysis with polarity reversal
EDI	-	Electrodeionization
EERO	-	Energy efficient reverse osmosis
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transmission infrared spectroscopy
f-$nTiO_2$	-	Functionalized nanoporous titanium oxide
f-TNT	-	Functionalized titanate nanotube
GA	-	Glutaraldehyde
GO	-	Graphene oxide
HCl	-	Hydrochloric acid
HNT	-	Halloysite nanotube
IP	-	Interfacial polymerization
IPC	-	Isophthaloyl dichloride
KBr	-	Potassium bromide

MED	-	Multiple effect distillation
MMM	-	Mixed matrix membrane
MPD	-	M-phenylenediamine
MSF	-	Multistage flash distillation
NaCl	-	Sodium chloride
N,N'-DMMPD	-	N,N'-dimethyl-m-phenylenediamine
NaOH	-	Sodium hydroxide
NF	-	Nanofiltration
$nTiO_2$	-	Nanoporous titanium oxide
PA	-	Polyamide
PES	-	Polyethersulfone
PIP	-	Piperazine
PVA	-	Polyvinyl alcohol
PSf	-	Polysulfone
PWF	-	Pure water flux
RO	-	Reverse osmosis
SDS	-	Sodium dodecyl sulfate
SIP	-	Sequential interfacial polymerization
SR	-	Sulfate removal
SSRO	-	Single stage reverse osmosis
SWRO	-	Seawater reverse osmosis
TEA	-	Triethylamine
TEM	-	Transmission electron microscopy
TFC	-	Thin film composite
TFN	-	Thin film nanocomposite
TiO_2	-	Titanium oxide
TMC	-	Trimesoyl chloride
TNT	-	Titanate nanotube
UF	-	Ultrafiltration
WHO	-	World Health Organization
XRD	-	X-ray diffraction

LIST OF SYMBOLS

A_m	-	Effective membrane surface area
C_f	-	Solute concentration in the feed solution
C_p	-	Solute concentration in the permeate solution
J	-	Membrane water flux
MW_{GA}	-	Molecular weight of GA
$MW_{PVAunit}$	-	Molecular weight of one PVA unit
ρ	-	Density
R	-	Membrane solute rejection
R_{ms}	-	Membrane root mean square roughness
V	-	Volume of permeate collected
W_{GA}	-	Weight of GA
W_{PVA}	-	Weight of PVA
X	-	Crosslinking degree of PVA
γ_L	-	Liquid surface tension
Υ	-	Surface tension
Δt	-	Experimental time for permeate collection
μ	-	Viscosity
θ	-	Equilibrium contact angle value
Δ	-	Relative membrane surface area
$-\Delta G_{SL}$	-	Surface corrected solid-liquid interfacial free energy

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Mankind has long been relying on natural freshwater resources for water supply. In ancient time, mankind withdrew water from the nature (i.e., rivers, lakes and groundwater aquifers) for domestic uses and irrigation purposes. Today, although the practice of sourcing water from the nature remains unchanged, the amount of water withdrawn has certainly increased, given i) the need to supply an appreciable amount of water to the industrial and manufacturing sectors, in addition to domestic uses and irrigation purposes as well as ii) the need to meet the needs of the ever-growing world population. In view of this, it may be reasonable to assume that the total water withdrawal from the nature will continue to rise in the future.

To put things into perspective, Wada and Bierkens (2014) estimated and projected the trends for total global water withdrawal, sectoral water consumption as well as groundwater abstraction from the 1960s to the 2100s, as shown in Figure 1.1. It can be seen that the total water withdrawal has increased remarkably from the 1960s until 2010, which is in line with the increase in sectoral water consumption. Moreover, it is projected that the sectoral water consumption and total water withdrawal will continue to rise, with no sign of levelling off until 2100.

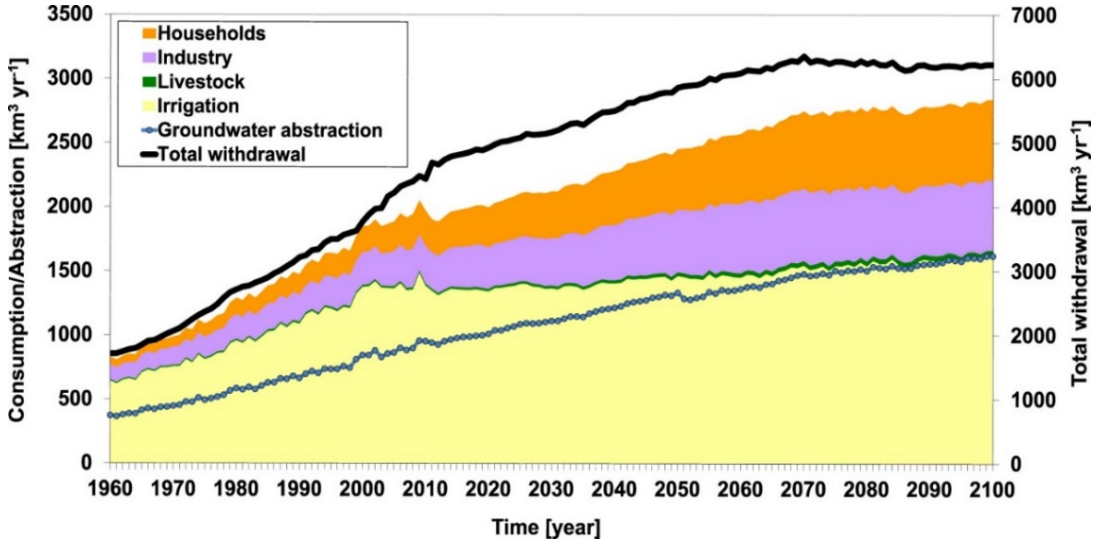

Figure 1.1: Estimated and projected trends of total blue water withdrawal, sectoral blue water consumption and total groundwater abstraction over the period from 1960 to 2100 (Wada and Bierkens, 2014).

Nonetheless, it is worth noting that freshwater supplies from the nature are finite, as only 0.007% of the total water on Earth is readily accessible by mankind. Additionally, it is also interesting to note that only 30% of the extracted water goes back directly into the surface waterways or groundwater, whereas the balance is either lost or consumed, thereby requiring wastewater treatment (Kürklü *et al*., 2017). Under these circumstances, when the water withdrawal rate is approaching the nature's self-replenishing rate, it may lead to an increase in water stress worldwide. Figure 1.2 depicts the water stress by country as projected by Luo et al. (2015) based on a series of reported and modelled global datasets. It clearly shows that more than half of the countries worldwide may experience critical water stress by year 2040 due to high water withdrawal and consumption rates.

In addition to high water withdrawal, the occurrence of climate change, as well as the pollution of freshwater sources due to anthropogenic activities are generally perceived as the contributing factors that will greatly reduce freshwater availability in years to come. In this regard, key players in the water industries should opt for more promising methods to augment the supply of freshwater, one of which is to tap on the unconventional water source – the ocean.

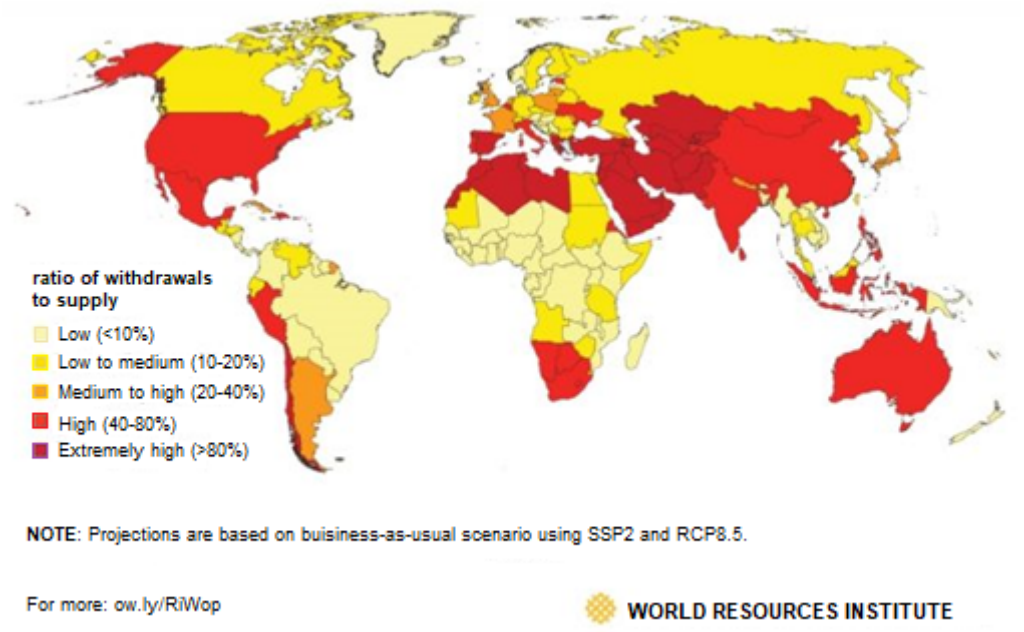

Figure 1.2: Water stress by country (Luo *et al*., 2015).

1.2 Saline Water Desalination

Over the years, there are two main technologies developed to desalinate saline water, which are the thermal and membrane technologies. These technologies have been proven to successfully remove >99% of salt from saline water, hence demonstrating the practicability of converting saline water into freshwater. For thermal technologies such as multi-stage flash and multi-effect distillation, desalination is achieved by heating saline water in a series of low pressure chambers and condensing water vapor into pure water. On the other hand, membrane technologies such as nanofiltration (NF) and reverse osmosis (RO) produce freshwater by pressurizing saline water through a series of thin sheet membranes that are capable of filtering out dissolved salts while allowing water molecules to pass through.

Although both methods are capable of desalinating saline water, membrane technologies are currently preferred over the thermal technologies. This is due to the recent cost hike in energy production, which renders thermal technology a costly method for freshwater production. Furthermore, extensive research in membrane

development has greatly reduce the cost for saline water desalination using membrane technologies. As of 30th June 2015, there are a total of 18,426 desalination plants installed across 150 countries worldwide, producing a sum of 22.9 billion US gallons of freshwater to support the usage of more than 300 million people (International Desalination Association, 2015). It is worth nothing that out of the total desalination plants installed, >60% are operating based on the RO technology (Figure 1.3).

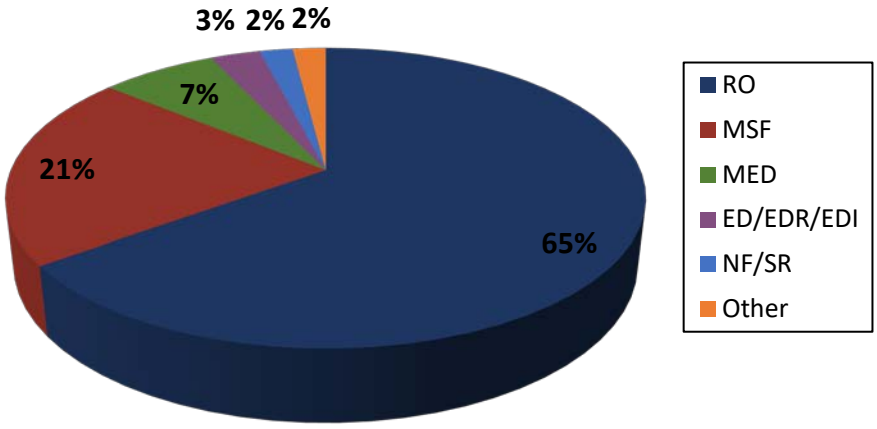

Figure 1.3: Distribution of total world installed capacity by technology (Burn *et al.*, 2015).

Current state-of-the-art membrane desalination plants are utilizing thin film composite (TFC) membranes for saline water desalination via RO processes. This type of membrane was firstly introduced by Cadotte and his colleagues back in the 1970s (Cadotte *et al.*, 1980) and has since made saline water desalination a feasible process worldwide. To date, TFC membrane serves as the benchmark for membrane development owing to i) its superior salt separating capabilities at a relatively high water permeability, ii) high pH, temperature and chemical tolerance, iii) high mechanical strength and iv) the possibility of optimizing the selective and support layers independently for desired performance enhancements. Nevertheless, further membrane improvements with respect to its water permeability (without jeopardizing its solute rejection capabilities), fouling and chlorine resistance are necessary to further improve the economics of the membrane desalination processes.

In the recent years, research spotlight for membrane development has been focused on the development of thin film nanocomposite (TFN) membranes that was introduced by Jeong and his colleagues back in year 2007 (Jeong *et al*., 2007). TFN membranes were reported to exhibit higher water permeability at similar salt rejection as the TFC membranes. Additionally, some TFN membranes were also demonstrated to exhibit better fouling and chlorine resistance. Albeit the enhanced separation performance of TFN membranes, there remains some rooms for improvements in its fabrication process as elucidated in the next sub-section.

1.3 Problem Statements

Both TFC and TFN membranes are fabricated using interfacial polymerization (IP) approach. In brief, IP process involves i) the contact and reaction of two monomers (an amine monomer (dissolved in water) and an acyl chloride monomer (dissolved in organic solvent)) atop a microporous support, thus forming the polyamide selective layer, followed by ii) membrane heat treatment to promote further membrane cross-linking and the removal of excess solvent. For the fabrication of TFN membranes, hydrophilic nanomaterials are commonly dispersed in the aqueous phase prior to the IP process. Nevertheless, it was demonstrated by Huang *et al*. (2013) that the dispersion of nanomaterial in the organic phase yielded membrane of better filtration performances in comparison to membrane formed by dispersing nanomaterial in the aqueous phase. However, the dispersion of hydrophilic nanomaterial in the organic solvent remains challenging owing to their incompatibilities.

To improve the dispersion of hydrophilic nanomaterials in organic solvent, Emadzadeh *et al*. (2015) and Lai *et al*. (2016) replaced the commonly used organic solvent (n-hexane) with cyclohexane in the membrane fabrication process. According to the authors, nanomaterials tended to disperse better in organic solvents of higher boiling point and viscosity. In view of this, Isoparaffin-G, an organic solvent with viscosity and boiling point even higher than cyclohexane could potentially be used for

even better nanomaterial dispersion. However, the effects of organic solvents on the separation performances of TFC membrane must be studied prior to the fabrication of TFN membranes. This is because both the IP reaction and membrane heat treatment conditions are dependent on the properties of the organic solvent (i.e., surface tension, viscosity and boiling point). Therefore in the first part of this study, the effects of organic solvent are investigated by fabricating a series of TFC membranes using four different types of organic solvents. Alongside the study of organic solvent, membrane heat treatment methods, post-IP treatment (prior to heat treatment) and the usage of additives are also investigated. It is anticipated that highly reproducible TFC membranes could be fabricated and serve as a stable baseline for comparison with the TFN membranes in the second part of this study.

For the fabrication of TFN membranes, some general basis for the selection of new nanomaterial in the fabrication of TFN membranes could be formulated with reference to the findings published in the literature. Generally, the nanomaterial should be i) highly hydrophilic, ii) negatively charged and iii) possessing pores or water channels. In addition to these criteria, it is worth noting that structure of the nanomaterial (i.e., size and shape) should also be taken into consideration. The effects of nanomaterial structure (same material with similar shapes but different sizes) on membrane performance was previously reported by Lind *et al*. (2009). Meanwhile, the effects of nanomaterial structure (considering same material with different sizes and shapes) on membrane performance, however, has not been discussed in the past.

In the second part of this study, experimental works are planned systematically to investigate the effects of nanomaterial structure (different sizes and shapes) on membrane separation performance. Additionally, membrane surface coating is studied to minimize surface defects that is likely to occur following the incorporation of nanomaterials. In addition to membrane water flux and salt rejection, boron rejection of all TFC and TFN membranes are evaluated to study the practicability of utilizing TFN membranes for saline water desalination.

1.4 Objectives

Looking at the research problems stated in the previous sub-section, the following objectives are formulated:

1. To study the effects of organic solvents, heat treatment methods, post-interfacial polymerization solvent rinsing and additives on the physicochemical properties and performance of TFC RO membranes for salt and boron removal.
2. To investigate the effects of nanomaterial structures and surface coating on salt and boron rejection of TFN RO membranes.

1.5 Research Scopes

To achieve the objectives of this study, the following scope of works are planned:

1. Fabricating TFC membranes via interfacial polymerization of MPD (2.0 wt/v%) and TMC (0.1 wt/v%) under three different heat treatment methods. These methods differ from one and another with respect to the total membrane surfaces exposed to heat treatment. In Method A, both the polyamide (PA) and substrate layer will be exposed to heat treatment. Comparatively, only the PA layer will be heat treated in Method B and C.
2. Characterizing the membrane surface hydrophilicity and morphology of TFC membranes formed in (1) using contact angle goniometer, field emission scanning electron microscopy (FESEM) as well as filtration performance against 2000 mg/L single salt solution (NaCl and/or $CaCl_2$) and 5 mg/L boric acid aqueous solution.
3. Fabricating two series of TFC membranes using four types of organic solvents (n-hexane, n-heptane, cyclohexane and Isoparaffin-G) by adopting the best heat treatment method discovered in (2). The TFC membranes are fabricated

by keeping one series of the membranes rinsed with pure n-hexane (prior to post-IP heat treatment) while another series without post-IP rinsing.

4. Fabricating TFC membrane by adding additives in the aqueous phase during membrane fabrication process for comparison with the best membrane obtained in (2).
5. Characterizing physicochemical properties and filtration performance of TFC membranes fabricated in (3) and (4).
6. Synthesizing nanoporous titanium oxide ($nTiO_2$) and titanate nanotube (TNT) using solvothermal and hydrothermal methods, respectively, followed by surface functionalization using 1-(2-amino-ethyl)-3-aminopropyl trimethoxysilane.
7. Characterizing the physicochemical properties of the synthesized nanomaterials using Fourier-transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and X-ray diffraction (XRD).
8. Fabricating TFN membranes by incorporating self-synthesized nanomaterials (at a fixed loading of 0.05 wt/v%) into membrane PA selective layer under the best IP conditions found in (5). Coating TFN membranes using 0.1 wt% polyvinyl alcohol (PVA) to heal possible defects formed following the incorporation of nanomaterials.
9. Characterizing possible changes to membrane surface roughness, morphology, functional groups and hydrophilicity following the incorporation of nanomaterials using atomic force microscopy (AFM), FESEM, FTIR and contact angle measurements. Evaluating membrane filtration performance against 2000 mg/L NaCl and 5 mg/L boric acid aqueous solution.

1.6 Significance of the Study

In the recent years, TFN membranes have been extensively studied for saline water desalination. Published research works have demonstrated improved membrane separation performances upon the incorporation of nanomaterials in the membrane selective layer. Nevertheless, there remains several challenges in the fabrication process of TFN membranes. These challenges and research gaps form the basis of this study. It is envisaged that the study on the role of nanomaterial structures would allow membrane researchers to form better basis for the selection of novel nanomaterial for TFN membrane fabrication. Also, it is anticipated that the study of TFC and TFN membrane fabrication conditions as well as membrane surface coating would contribute to the fabrication of TFN membranes with consistent and superior separation performances for saline water desalination, thereby reducing the cost of saline water desalination. Furthermore, this study would allow membrane researchers to understand the effects of nanomaterials incorporation in TFN membrane boron rejection and the practicability of utilizing TFN membranes in saline water desalination.

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