UNIVERSITY
OF TECHNOLOGY
SYDNEY

DEVELOPMENT OF THIN-FILM COMPOSITE MEMBRANES INCORPORATED WITH GRAPHENE OXIDE AND DERIVATIVES FOR FORWARD OSMOSIS PROCESSES

by Nawshad Akther

Thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

under the supervision of Prof. Hokyong Shon and Dr. Sherub Phuntsho

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September 2020

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, **Nawshad Akther**, declare that this thesis is submitted in fulfilment of the requirements for the award of **Doctor of Philosophy**, in the **School of Civil and Environmental Engineering/ Faculty of Engineering and Information Technology** at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

This research is supported by the Australian Government Research Training Program.

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(Nawshad Akther)

Date: 4th September 2020

DEDICATION

This thesis is dedicated wholeheartedly to:

My beloved parents, Zinnat and Jahangir,
who have always supported me, showed me the power of education and been the source of my inspiration,

and

My husband, Ashique,
for having my back, motivating me and sharing the path with me.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to those who have supported me along this long but fulfilling journey towards the completion of my PhD thesis.

Foremost, I would like to express my heartfelt gratitude to my principal supervisor, Prof. Hokyong Shon, for his great mentorship, professional advice, encouragement, endless support and bringing out the best in me throughout my PhD study. I would also like to convey my gratitude to my co-supervisor, Dr. Sherub Phuntsho, for his insightful comments and valuable feedback during my study. Their consistent guidance and support throughout my PhD study have been invaluable, motivated me to grow as a researcher and give my best towards the completion of this thesis.

Besides my supervisors, I would like to acknowledge the support I received from the external collaborators who provided me with the opportunity to work with them. I would like to thank Prof. Hideto Matsuyama and Prof. Tomohisa Yoshioka for inviting me to work as a Visiting Researcher at Kobe University and use their laboratories and research facilities at the Research Center for Membrane and Film Technology. I further acknowledge Prof. Noreddine Ghaffour at King Abdullah University of Science and Technology (KAUST), Prof. Yuan Chen at The University of Sydney, A/Prof. Tae-Hyun Bae at Korea Advanced Institute of Science and Technology (KAIST) and Claus Helix-Nielsen at the Technical University of Denmark for their collaboration and support in my research work. I also appreciate Shengyao Wang and Yuki Kawabata at Kobe University, Ziwen Yuan at The University of Sydney, Victoria Sanahuja-Embuena and Radosław Górecki at the Technical University of Denmark for their contribution to my collaboration research projects.

Moreover, I am grateful to Dr. Sungil Lim for developing my membrane fabrication skills and Dr. Md. Johir and Dr. Niren Pathak for their assistance in the laboratory. My heartfelt appreciation goes to my friends in UTS and everyone in the NanoMemPro group, especially Van Huy Tran, Minwei Yao, Syed Muztuza Ali, Pema Dorji and Mukit Hossain for making my time enjoyable and helping me keep up my momentum during the entire course of my PhD journey.

I want to acknowledge the full financial support that I received from the Australian Government Research Training Program (RTP) to complete my PhD study.

Finally, I would like to thank my parents and my father-in-law for making me recognize the importance of education and hard work, making my academic journey a success, motivating me to pursue my dreams and be independent. I want to express my deep appreciation for the continuous support and encouragement that I have received from my brothers, Javed and Abed. I am grateful to my husband, Ashique, for believing in my ability to succeed and fulfil my dreams and for his enduring optimism despite the challenges we confronted during my PhD journey. Without his support, cooperation and motivation, it would have been difficult to accomplish my research goals.

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LIST OF PUBLICATIONS

This list includes journal articles that have been prepared during the PhD candidature, which are either *part of or **not part of the thesis.

1. ****Akther, N**., Lim, S., Tran, V.H., Phuntsho, S., Yang, Y., Bae, T.-H., Ghaffour, N. & Shon, H.K. 2019, 'The effect of Schiff base network on the separation performance of thin film nanocomposite forward osmosis membranes', *Separation and Purification Technology*, vol. 217, pp. 284-93.
2. ***Akther, N.**, Phuntsho, S., Chen, Y., Ghaffour, N. & Shon, H.K. 2019, 'Recent advances in nanomaterial-modified polyamide thin-film composite membranes for forward osmosis processes', *Journal of Membrane Science*, vol. 584, pp. 20-45. **(Chapter 2)**
3. **Yao, M., Ren, J., **Akther, N.**, Woo, Y.C., Tijing, L.D., Kim, S.-H. & Shon, H.K. 2019, 'Improving membrane distillation performance: Morphology optimization of hollow fiber membranes with selected non-solvent in dope solution', *Chemosphere*, vol. 230, pp. 117-26.
4. **Tran, V.H., Lim, S., Han, D.S., Pathak, **N., Akther**, N., Phuntsho, S., Park, H. & Shon, H.K. 2019, 'Efficient fouling control using outer-selective hollow fiber thin-film composite membranes for osmotic membrane bioreactor applications', *Bioresource Technology*, vol. 282, pp. 9-17.
5. **Lim, S., Tran, V.H., **Akther, N.**, Phuntsho, S. & Shon, H.K. 2019, 'Defect-free outer-selective hollow fiber thin-film composite membranes for forward osmosis applications', *Journal of Membrane Science*, vol. 586, pp. 281-91.
6. ***Akther, N.**, Yuan, Z., Chen, Y., Lim, S., Phuntsho, S., Ghaffour, N., Matsuyama, H. & Shon, H.K. 2020, 'Influence of graphene oxide lateral size on the properties

and performances of forward osmosis membrane', *Desalination*, vol. 484, p. 114421. **(Chapter 5)**

7. **Lim, S., Park, K.H., Tran, V.H., **Akther, N.**, Phuntsho, S., Choi, J.Y. & Shon, H.K. 2020, 'Size-controlled graphene oxide for highly permeable and fouling-resistant outer-selective hollow fiber thin-film composite membranes for forward osmosis', *Journal of Membrane Science*, vol. 609, p. 118171.
8. ***Akther, N.**, Ali, S.M., Phuntsho, S. & Shon, H.K. 2020, 'Surface modification of thin-film composite forward osmosis membranes with polyvinyl alcohol–graphene oxide composite hydrogels for anti-fouling properties', *Desalination*, vol. 491, p. 114591. **(Chapter 4)**
9. **Lim, S., **Akther, N.**, Tran, V.H., Bae, T.-H., Phuntsho, S., Merenda, A., Dumée, L.F. & Shon, H.K. 2020, 'Covalent organic framework incorporated outer-selective hollow fiber thin-film nanocomposite membranes for osmotically driven desalination', *Desalination*, vol. 485, p. 114161.
10. **Shen, Q., Lin, Y., Kawabata, Y., Jia, Y., Zhang, P., **Akther, N.**, Guan, K., Yoshioka, T., Shon, H.K., Matsuyama, H. 2020, 'Engineering heterostructured thin-film nanocomposite membrane with functionalized graphene oxide quantum dots (GOQD) for highly efficient reverse osmosis', *ACS Applied Materials & Interfaces*, vol. 12, no. 34, pp. 38662-73.
11. **Daer, S[†]., **Akther, N.**[†], Wei, Q., Shon, H.K. & Hasan, S.W. 2020, 'Influence of silica nanoparticles on the desalination performance of forward osmosis polybenzimidazole membranes', *Desalination*, vol. 491, p. 114441.
12. ****Akther, N.**, Lin, Y., Matsuyama, H., Phuntsho, S., Ghaffour, N. & Shon, H.K. 2020, 'In situ coating of ultrathin silica layer on polyamide thin-film composite

forward osmosis membranes for enhanced separation and anti-fouling properties', accepted in *Journal of Membrane Science*.

13. ***Akther, N.**, Sanahuja-Embuena, V., Górecki, R., Phuntsho, S., Helix-Nielsen, C. & Shon, H.K. 2020, 'Employing the synergistic effect between aquaporin nanostructures and graphene oxide for enhanced separation performance of thin-film nanocomposite forward osmosis membranes', *Desalination*, vol. 498, p. 114795 **(Chapter 6)**
14. ***Akther, N.**, Kawabata, Y., Lim, S., Yoshioka, T., Matsuyama, H., Phuntsho, S. & Shon, H.K. 2020, 'Effect of graphene oxide quantum dots on the interfacial polymerization of a thin-film nanocomposite forward osmosis membrane: An experimental and molecular dynamics study', *Journal of Membrane Science*, vol. 630, p. 119309 **(Chapter 7)**

CONFERENCE PRESENTATIONS

Some parts of this study have been presented in conferences as listed below:

1. **Akther, N.**, Lim, S., Tran, V.H., Phuntsho, S., Bae, T.-H, Ghaffour, N. & Shon, H.K. 'Covalent organic frameworks-based thin-film nanocomposite membranes for forward osmosis processes', The 11th conference on the Aseanian Membrane Society, AMS11, July 3–6, Brisbane, Australia, 2018.
2. Lim, S., Tran, V.H., **Akther, N.**, Phuntsho, S. & Shon, H.K. 'Preparation of outer-selective thin-film composite hollow fiber membranes with high performance and fouling resistance for forward osmosis applications', The 11th conference on the Aseanian Membrane Society, AMS11, July 3–6, Brisbane, Australia, 2018.
3. Shon, H.K. & **Akther, N.** 'Carbon-based nanomaterial incorporated FO membranes', International Workshop for Membrane at Kobe University in 2019 (iWMK2019), November 18-19, Kobe, Japan, 2019.
4. **Akther, N.**, Phuntsho, S. & Shon, H.K. 'Influence of graphene oxide lateral size on the properties and performances of forward osmosis membrane', 4th International Conference on Desalination using Membrane Technology (MEMDES), December 1-4, Perth, Australia, 2019.
5. **Akther, N.**, Sanahuja-Embuena, V., Górecki, R., Phuntsho, S., Helix-Nielsen, C. & Shon, H.K. 'Employing the synergistic effect between aquaporin nanostructures and graphene oxide for enhanced separation performance of thin-film nanocomposite forward osmosis membranes', Membrane Society of Australasia (MSA) Annual General Meeting and Conference, November 23-24, Clayton, Victoria, 2020.

PREFACE

This doctoral thesis is prepared in a “Thesis by compilation” format according to the “Graduate Research Candidature Management, Thesis Preparation and Submission Procedures, 2019” of the University of Technology Sydney. It comprises of the articles that have been published or submitted for publication.

This thesis contains one published review paper in Chapter 2 and four original research articles in Chapters 4 through 7, three of which are published and one accepted for publication. The authorship of these works has been decided after discussing with the supervisory team.

Chapter 2 comprises of the following article:

Akther, N., Phuntsho, S., Chen, Y., Ghaffour, N. & Shon, H.K. 2019, ‘Recent advances in nanomaterial-modified polyamide thin-film composite membranes for forward osmosis processes’, *Journal of Membrane Science*, vol. 584, pp. 20-45.

Chapter 4 includes the following article:

Akther, N., Ali, S.M., Phuntsho, S. & Shon, H.K. 2020, ‘Surface modification of thin-film composite forward osmosis membranes with polyvinyl alcohol–graphene oxide composite hydrogels for anti-fouling properties’, *Desalination*, vol. 491, p. 114591.

Chapter 5 is based on the following technical paper:

Akther, N., Yuan, Z., Chen, Y., Lim, S., Phuntsho, S., Ghaffour, N., Matsuyama, H. & Shon, H.K. 2020, ‘Influence of graphene oxide lateral size on the properties and performances of forward osmosis membrane’, *Desalination*, vol. 484, p. 114421.

Chapter 6 is published in *Desalination*:

Akther, N., Sanahuja-Embuena, V., Górecki, R., Phuntsho, S., Helix-Nielsen, C. & Shon, H.K. 2021, 'Employing the synergistic effect between aquaporin nanostructures and graphene oxide for enhanced separation performance of thin-film nanocomposite forward osmosis membranes', *Desalination*, vol. 498, p. 114795.

Chapter 7 is published in *Journal of Membrane Science:*

Akther, N., Kawabata, Y., Lim, S., Yoshioka, T., Phuntsho, S., Matsuyama, H. & Shon, H.K. 2021, 'Effect of graphene oxide quantum dots on the interfacial polymerization of a thin-film nanocomposite forward osmosis membrane: An experimental and molecular dynamics study', *Journal of Membrane Science,* vol. 630, p. 119309.

LIST OF ABBREVIATIONS

AAPTS	1-(2-amino-ethyl)-3-aminopropyl] trimethoxysilane
AFM	Atomic force microscopy
Ag	Silver
AgNP	Silver nanoparticles
AL-DS	Active layer oriented towards draw solution
AL-FS	Active layer oriented towards feed solution
Al_2O_3	Aluminium oxide
AQN	Aquaporin Z reconstituting nanostructures
AqpZ	Aquaporin Z
ASP	Alternate soaking process
BP	Bucky paper
BSA	Bovine serum albumin
$CaCO_3$	Calcium carbonate
CFV	Cross-flow velocity
CN	Graphitic carbon nitride
CNT	Carbon nanotube
CTA	Cellulose triacetate
DA	Dopamine
DI	De-ionized water
DS	Draw solution
ECP	External concentration polarisation
Fe_3O_4	Iron (III) oxide
FO	Forward osmosis
FRR	flux recovery ratio

FS	Feed solution
FTIR	Fourier transform infrared spectroscopy
GA	Glutaraldehyde
GO	Graphene oxide
GQD	Graphene/ graphene oxide/ carbon quantum dot
HA	Humic acid
HF	Hollow fiber
HTI	Hydration technologies Inc.
HNT	Halloysite nanotube
ICP	Internal concentration polarisation
INT	Imogolite nanotube
IEP	Isoelectric point
IP	Interfacial polymerization
ISHF	Inner-selective hollow fiber
LbL	Layer-by-layer
LDH	Layered double hydroxide
MD	Molecular dynamics/ Membrane distillation
MOF	Metal-organic framework
MPD	1,2-phenylenediamine
NaCl	Sodium chloride
NF	Nanofiltration
NIPS	Non-solvent induced phase separation
NMP	1-methyl-2-pyrrolidone
NP	Nanoparticles
OMBR	Osmotic membrane bioreactor
OSHF	Outer-selective hollow fiber
PA	Polyamide

PAN	Polyacrylonitrile
pDA	Polydopamine
PEG	Polyethylene glycol
PEG-PPG-PEG	Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)
PES	Poly(ethersulfone)
PEI	Polyethylenimine
PET	Polyester
PI	Phase inversion
PMA	Poly(ether monoamine)
PRO	Pressure-retarded osmosis
PLL	Poly L-Lysine
PMR	Photocatalytic membrane reactor
PSf	Polysulfone
PV	Pervaporation
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
PVP	Polyvinylpyrrolidone
rGO	Reduced graphene oxide
RO	Reverse osmosis
SA	Sodium alginate
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope
SiO_2	Silica
TDS	Total dissolved solids
TEA	Triethylamine
TFC	Thin-film composite

TFC-P	PVA hydrogel-coated TFC membrane
TFC-PGO	PVA-GO hydrogel-coated TFC membrane
TFN	Thin-film nanocomposite
TiO_2	Titanium oxide
TMC	Trimesoyl chloride
TNT	Titanate nanotubes
TSB	Tryptic soy broth
UF	Ultrafiltration
UiO-66	Zirconium (IV) carboxylate metal organic framework
VAIP	Vacuum-assisted interfacial polymerization
Zn_2GeO_4	Zinc germinate
ZnO	Zinc oxide
ZSCSNP	ZnO-SiO_2 core-shell nanoparticles

NOMENCLATURE

Symbol	Meaning	Unit
ΔC	Concentration difference across the selective layer of the membrane	$mg \cdot L^{-1}$
ΔC_{FS}	Change in the feed solution concentration after an interval of Δt	$mg \cdot L^{-1}$
ΔP	Transmembrane pressure	Pa
Δt	Time interval	h
ΔV_{FS}	Change in the feed solution volume during the performance test	L
μ	Solution viscosity	Pa·s
χ_{CL}	Theoretical cross-linking degree	%
A	Pure water permeability coefficient	$L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$
A_m	Effective area of membrane	m^2
B	Solute permeability coefficient	$L \cdot m^{-2} \cdot h^{-1}$
B/A	Intrinsic membrane selectivity	bar
C_{FS}	Bulk feed solution concentration	$mol \cdot L^{-1}$
C_{DS}	Bulk draw solution concentration	$mol \cdot L^{-1}$
D	Diffusion coefficient	$m^2 \cdot s^{-1}$
F	Osmotic pressure across the membrane	Pa
J_s	Reverse solute flux	$g \cdot m^{-2} \cdot h^{-1}$ (gMH)
J_w	Water flux	$L \cdot m^{-2} \cdot h^{-1}$ (LMH)
$J_{w,0}$	Baseline water flux	$L \cdot m^{-2} \cdot h^{-1}$
$J_w/J_{w,0}$	Normalized flux	---
M	Molar concentration	$mol \cdot L^{-1}$
MSD	Mean square displacement	---

MW_{CL}	Molecular weight of the cross-linking agent	g·mol^{-1}
$MW_{PVA\,unit}$	Molecular weight of one PVA unit	g·mol^{-1}
N_{ion}	Ionization number in water	---
R	Overall hydraulic resistance against the water permeation	m^{-1}
R_a	Mean value of membrane surface roughness	nm
R_f	Foulant resistance	m^{-1}
R_g	Universal gas constant	Pa·K^{-1}·mol^{-1}
R_m	Membrane resistance	m^{-1}
R_{max}	Maximum value of membrane surface roughness	nm
R_q	Root mean square value of membrane surface roughness	nm
S	Structural parameter	μm
$SRSF\ (J_s/J_w)$	Specific reverse solute flux	g·L^{-1}
T	Solution temperature	K
V_{FS}	Feed solution volume	L
W_{CL}	Weight of cross-linking agent	g
W_{PVA}	Weight of PVA	g

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ABSTRACT

Polyamide (PA) thin-film composite (TFC) membranes have attained much attention for separation processes like water treatment, wastewater reclamation and desalination due to their superior intrinsic properties, such as high salt rejection and water permeability compared to the first generation of cellulose-based membranes. Nonetheless, several problems like fouling and trade-off between membrane selectivity and water permeability hinder the progress of conventional PA TFC forward osmosis (FO) membranes for real applications. To overcome these issues, nanomaterials have been integrated into the TFC membranes. Nanomaterial-modified membranes have demonstrated significant improvement in their anti-fouling properties and performance. Besides, PA TFC membranes can be designed for targeted applications like heavy metal removal and osmotic membrane bioreactor by using specific nanomaterials to modify their physicochemical properties (porosity, surface charge, hydrophilicity, membrane structure and mechanical strength). However, poor compatibility between nanomaterial and polymer matrix can result in poor membrane stability and selectivity. Hence, it is important to improve the stability of nanocomposite membranes to enable their successful application. Therefore, this doctoral study aims to modify the TFC membranes using graphene oxide (GO) derivatives for FO processes. Different TFC membrane and GO modification techniques have been employed and extensively characterized to understand and possible interaction between GO and TFC membranes to overcome and explain the existing challenges.

Firstly, the PA layer of commercial TFC FO membrane was coated with glutaraldehyde cross-linked polyvinyl alcohol (PVA) hydrogel solution comprising of GO at various loadings to enhance their fouling resistance. Experimental results showed that the

PVA/GO coating improved the smoothness and hydrophilicity of the membrane surface. PVA hydrogel with an optimal GO loading of 0.02 wt% showed a 55% reduction in specific reverse solute flux (*SRSF*), only a marginal reduction in the water flux, and the best anti-fouling property with a 58% higher flux recovery compared to the pristine TFC membrane. The significant improvement in the selectivity of the modified membranes meant that the hydrogel coating could be used to seal PA defects. The addition of GO flakes in PVA hydrogel coating also improved the biofouling resistance of the modified membranes, which can be attributed to the biocidal activity of GO and the superior surface properties and morphology of the modified membranes arising from hydrophilic PVA coating.

Following the surface modification of commercial TFC FO membranes with PVA/GO hydrogel, the effect of GO flake lateral size on the PA layer formation, TFC membrane properties and performance was investigated. GO suspensions with an average flake size ranging from 0.01 to 1.06 μm^2 were prepared by varying the sonication duration. It was observed that the large GO flakes obstructed the reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) monomers during the interfacial polymerization (IP) process by creating impervious regions that deteriorated membrane performance by forming defective PA layer formation. Whereas, smaller GO flakes were distributed more uniformly in the PA layer, creating fewer defects and demonstrating better desalination performance and anti-fouling property than the thin-film nanocomposite (TFN) membranes modified with larger GO flakes. The *SRSF* and water flux of the GO-modified TFN membranes improved by over 60% and 50%, respectively, when the average GO flake size was reduced from 1.06 to 0.01 μm^2 due to the formation of a thinner and more uniform PA layer. Our findings showed that a smaller GO flake size could be beneficial for minimizing PA layer defects.

After establishing that large GO flakes increase PA defects and deteriorate membrane selectivity, Aquaporin Z (AqpZ) reconstituting nanostructures (AQN) were embedded in the PA layer of GO TFN membranes to enhance their FO separation performance. The effect of increasing GO loading while retaining the AQN at an optimal loading of 0.2 wt% in the PA layer was investigated. Experimental results showed that GO flakes increased membrane water flux but decreased selectivity; whereas, AQN increased membrane selectivity by reducing the PA defects created by the GO flakes. As a consequence of favourable synergies between GO and AQN, the GO/AQN-incorporated TFN membranes demonstrated significantly higher *SRSF* while retaining the water permeability compared to the GO-incorporated TFN membranes. The TFN50 membrane with 0.2 wt% AQN and 0.005 wt% GO loading showed almost 3 folds increase in water flux (24.1 $L \cdot m^{-2} \cdot h^{-1}$) in comparison to the TFC membrane (8.2 $L \cdot m^{-2} \cdot h^{-1}$), while retaining membrane selectivity (0.37 $g \cdot L^{-1}$). However, the TFN50 membrane demonstrated a 27% lower *SRSF* and a marginal increase in water flux than the TFNGO50 membrane embedded with 0.005 wt% GO and no AQN. It was concluded that the synergistic effect of GO and aquaporin facilitated enhancement in both the membrane permeability and selectivity.

Finally, graphene oxide quantum dots (GQD) were used for their small size (< 5 nm) to improve the FO performance of outer-selective hollow fiber (OSHF) TFC membranes fabricated using the vacuum-assisted interfacial polymerization (VAIP) technique. Both experimental and molecular dynamics (MD) simulation proved that the GQD loading could influence both the IP process and the water transport across the PA layer. The TFN5 membrane with an optimal GQD loading of 5 $mg \cdot L^{-1}$ demonstrated a 64% lower *SRSF* (0.12 $g \cdot L^{-1}$) and 68% higher water flux (30.9 $L \cdot m^{-2} \cdot h^{-1}$) compared to the TFC membrane due to its improved hydrophilicity and creation of more water channels inside the PA layer after addition of GQDs. MD simulation was also employed at water-hexane and water-PA interface to investigate the effect of GQD loading on the IP reaction and membrane separation performance. The MD simulation results showed that a very high loading of GQDs could result in their aggregation at the water-hexane interface during the IP reaction and form a defective PA layer. It was also found that uniform dispersion of GQDs inside the PA layer can increase the water diffusivity inside the membrane leading to high water permeability, but too high GQD density can reduce the membrane water permeability by GQDs acting as barriers to water transport.

Overall, this study considered various strategies to improve the performance of GO-incorporated PA TFC and TFN membrane by investigating the factors that govern water transport across the membranes. The findings of this study could deliver strategies for future improvements in GO-based PA TFC membranes.