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The Research Grants Council of Hong Kong
NSFC/RGC Joint Research Scheme
Joint Completion Report

(Please attach a copy of the completion report submitted to the NSFC by the Mainland researcher)

Part A: The Project and Investigator(s)

1. Project Title

Construction and mechanism of supertough/superwetting nanocrystalline interface on flexible polymeric membranes for water/oil separation

2. Investigator(s) and Academic Department/Units Involved

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Professor Tang Chuyang	Professor Liu Fu
Post	Professor	Professor
Unit / Department / Institution	Department of Civil Engineering, the University of Hong Kong	Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences
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Co-investigator(s) *(with title and institution)*	Dr. Wang Jianqiang * Dr. Yang Zhe (The University of Hong Kong)	Dr. Xiong Zhu Mr. Lin Haibo Mr. Wu Ziyang Mr. Chen Yongliang (Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences)

Note: * Dr. Wang Jianqiang has left HKU, and he now works as an Associate Professor at Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences. He continues to involve in the project as a member of the mainland team.

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted)*
Project Start date	01/01/2017	N.A.	N.A.
Project Completion date	31/12/2020	N.A.	N.A.
Duration *(in month)*	48	N.A.	N.A.
Deadline for Submission of Completion Report	31/12/2021	N.A.	N.A.

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. *To develop strategies to control the micro- and nano-scale surface morphology of poly(vinylidene fluoride) (PVDF) microporous membranes;*

2. *To realize the self-assembly of functional nanoparticles within the confinement pore structure of PVDF microporous membranes in order to impart supertough/superwetting performance to these membranes;*

3. *To investigate the fundamental mechanisms and principles governing the polymer-nanoparticle interaction and their stability during long term oil/water separation.*

5.2 Revised Objectives

Date of approval from the RGC: N.A.

Reasons for the change: N.A.

6. Research Outcome

<u>Major findings and research outcome</u>

- *Creation of high-permeance and superwetting membranes*. Electrospinning is found to be a highly effective method to obtain membranes with high porosity, large surface area, and excellent membrane permeance (Qing et al. 2017; Guo et al. 2021). By the careful choices of materials (e.g., hydrophobic materials such as PVDF (Qing et al. 2019) and polytetrafluoroethylene (Qing et al. 2017) or hydrophilic materials such as polyvinyl alcohol (PVA) (Qing et al. 2020a)), we obtained high-performance superwetting membranes that can be used for efficient oil/water separation.

- *Creation of surface morphology/roughness*. The oil/water separation and antifouling performance of the superwetting membranes can be further enhanced by the tailoring and control of membrane surface morphology. Several novel strategies have been developed during the project. For example, we discovered a new mechanism to create surface roughness on PVDF membranes via solvent-thermal induced roughening (STIR) method (Qing et al. 2018; Qing et al. 2019). The STIR method relies on the mismatched thermal expansion between a solvent-swelled polymer shell (larger thermal expansion) and the swelled core (smaller thermal expansion), resulting in controllable surface roughening effect (Qing et al. 2019). In another approach (Wang et al. 2021), a PVDF membrane with a dual-scale hyperporous structure is fabricated via dual-phase separation (vapor and nonsolvent). With the aid of additional in situ polymerization of poly(hydroxyethyl methylacrylate), the resultant membrane achieved a continuous "nonfouling" separation for oil/water emulsions via membrane demulsification.

- *Membrane surface modification and growth of nanoparticles*. Several effective methods have been developed to grow nanoparticles on microporous membranes, such as SiO_2 nanoparticles, TiO_2 nanoparticles, and TiO_2 nanofins (Qing et al. 2020a; Li et al. 2019). These hydrophilic surface decorations significantly enhanced the hydrophilicity and superwetting ability of the modified membranes, which greatly enhances their separation efficiency (permeance and retention properties) and antifouling performance. For example, we developed a simple electrospinning/in-situ growth strategy to prepare superhydrophilic-underwater-superoleophobic SiO2@PVA nanofibrous membranes for gravity-driven separation of oil/water mixture. The abundant hydroxyl groups on PVA nanofibers enabled uniform and stable deposition of silica nanoparticles, thus simultaneously realizing high surface energy surface (due to hydrophilic nature of PVA and silica) and multi-scale roughness features. The SiO2@PVA membranes exhibited efficient separation for both free oil/water mixture and a variety of surfactant-stabilized oil-in-water emulsions in a gravity-driven filtration process.

- *Oil/water separation*. The novel membranes developed in this project were tested for oil-water separation. The experimental results validated their antifouling performance and durability. The tailored interactions between oil/water mixture, membrane materials, and nanoparticles resulted in stable membrane separation performance.

Potential for further development of the research and the proposed course of action *(maximum half a page)*

The current project has primarily focused on the development of microporous membranes and its applications for oil/water separation. The research consortium will further develop this porous membrane technology to suit for a wide range of applications:

1. Water purification. The research consortium will explore the use of membrane technology for efficient contaminant removal from water, through sieving, adsorption, catalysis, and their combinations. For example, our primary results show efficient capture of toxic chemicals such as halogenated acetic acids, perfluorinated surfactants, etc. by carefully designed nanofibrous membranes. An undergraduate final year project student has been engaged to further work on the topic.
2. Air filtration. We intend to adapt the nano-/micro-structural design of membranes for the fabrication of high-efficiency air filters. We plan to submit a new proposal to Innovation and Technology Commission for potential funding of this further development.
3. Biomedical applications. The HK team is currently discussing with the Mainland team on the potential applications of membrane technology to biomedical applications, such as the separation, purification, and/or enrichment of active pharmaceutical ingredients (e.g., for vaccine development). A joint proposal will be prepared for the further development of this research direction.

7. The Layman's Summary

(describe in layman's language the nature, significance and value of the research project, in no more than 200 words)

Polymeric microporous membranes have been widely applied for the separation of micro-emulsions. However, long term exposure to unfavorable stress and water chemistry conditions can lead to irreversible damages due to creeping of membrane materials, resulting in the loss of superwetting and separation performance. This project aims to develop a supertough and superwetting interface on flexible polymeric membranes and to apply the resulting membranes for efficient oil/water separation. A primary micro-/nano-porous interface was prepared through phase inversion and template method on a poly(vinylidene fluoride) (PVDF) microporous membrane. Superwetting properties was introduced to this interface via (1) the growth of secondary hierarchical structures and (2) assembly of nanoparticles. The integration of the primary structure and nanoparticles resulted in a supertough and superwetting interface with controllable thickness. The resulting membranes show high separation efficiency, excellent antifouling performance, good retention properties, and satisfactory long-term performance for oil-water separation. This project provides fundamental insights into the design and fabrication of durable superwetting membranes as well as mechanisms governing the performance of membrane-based oil/water separation.

Part C: Research Output

8. Peer-reviewed journal publication(s) arising directly from this research project

(Please attach a copy of each publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.)

The Latest Status of Publications				Author(s) (***bold** the authors belonging to the project teams and denote the corresponding author with an asterisk**)	Title and Journal/ Book *(with the volume, pages and other necessary publishing details specified)*	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*	Accessible from the institutional repository *(Yes or No)*
Year of publication	Year of Acceptance *(For paper accepted but not yet published)*	Under Review	Under Preparation *(optional)*						
2021				**Wang, J. ***; He, B.; Ding, Y.; Li, T.; Zhang, W.; Zhang, Y.; **Liu, F. *; Tang, C. Y.**	Beyond superwetting surfaces: dual-scale hyperporous membrane with rational wettability for "nonfouling" emulsion separation via coalescence demulsification. *ACS Applied Materials & Interfaces* **2021,** *13*, (3), 4731-4739.	No	Yes	Yes	Yes
2021				**Guo, H.**; Zhang, J.; **Peng, L. E.**; Li, X.; Chen, Y.; **Yao, Z.**; Fan, Y.; Shih, K.; **Tang, C. Y. ***	High-efficiency capture and recovery of anionic perfluoroalkyl substances from water using PVA/PDDA nanofibrous membranes with near-zero energy consumption. *Environmental Science & Technology Letters* **2021,** *8*, (4), 350-355.	No	Yes	Yes	Yes

2020 (a)				**Qing, W.;** Li, X.; Wu, Y.; **Shao, S.; Guo, H.**; Yao, Z.; Chen, Y.; Zhang, W.; **Tang, C. Y.***	In situ silica growth for superhydrophilic-underwater superoleophobic Silica/PVA nanofibrous membrane for gravity-driven oil-in-water emulsion separation. Journal of Membrane Science 2020, 612, 118476.	No	Yes	Yes	Yes
2020 (b)				**Qing, W.;** Wu, Y.; Li, X.; Shi, X.; **Shao, S.**; Mei, Y.; Zhang, W.; **Tang, C. Y.***	Omniphobic PVDF nanofibrous membrane for superior anti-wetting performance in direct contact membrane distillation. *Journal of Membrane Science* **2020,** *608*, 118226.	No	Yes	Yes	Yes
2019				**Qing, W.; Wang, J.; Ma, X.; Yao, Z.;** Feng, Y.; Shi, X.; **Liu, F.**; Wang, P.; **Tang, C. Y. ***	One-step tailoring surface roughness and surface chemistry to prepare superhydrophobic polyvinylidene fluoride (PVDF) membranes for enhanced membrane distillation performances. *Journal of Colloid and Interface Science* **2019,** *553*, 99-107.	No	Yes	Yes	Yes
2019				Li, X.; **Qing, W.**; Wu, Y.; **Shao, S.; Peng, L. E.**; Yang, Y.; Wang, P.; **Liu, F.; Tang, C. Y. ***	Omniphobic nanofibrous membrane with pine-needle-like hierarchical nanostructures: toward enhanced performance for membrane distillation. *ACS Applied Materials & Interfaces* **2019,** *11*, (51), 47963-47971.	No	Yes	Yes	Yes

2019				He, B.; Ding, Y.; **Wang, J. *; Yao, Z.; Qing, W.**; Zhang, Y. *; **Liu, F. *; Tang, C. Y.**	Sustaining fouling resistant membranes: Membrane fabrication, characterization and mechanism understanding of demulsification and fouling-resistance. *Journal of Membrane Science* **2019,** *581*, 105-113.	No	Yes	Yes	Yes
2019				Ding, Y.; Wu, J.; **Wang, J.*; Lin, H.**; Wang, J.; Liu, G.; Pei, X.; **Liu, F.*; Tang, C. Y.**	Superhydrophilic and mechanical robust PVDF nanofibrous membrane through facile interfacial Span 80 welding for excellent oil/water separation. *Applied Surface Science* **2019,** *485*, 179-187.	No	Yes	Yes	Yes
2019				Zhou, S.; **Liu, F.; Wang, J.*; Lin, H.**; Han, Q.; Zhao, S.*; **Tang, C. Y.**	Janus Membrane with Unparalleled Forward Osmosis Performance. *Environmental Science & Technology Letters* **2019,** *6,* (2), 79-85.	2018	No	Yes	Yes
2018				**Qing, W.;** Shi, X.; Zhang, W.; **Wang, J.;** Wu, Y.; Wang, P.; **Tang, C. Y.***	Solvent-thermal induced roughening: A novel and versatile method to prepare superhydrophobic membranes. *Journal of Membrane Science* **2018,** *564*, 465-472.	2018	No	Yes	Yes
2018				Li, T.; **Liu, F.***; Zhang, S.; Lin, H.; **Wang, J.; Tang, C. Y.**	Janus polyvinylidene fluoride membrane with extremely opposite wetting surfaces via one single-step unidirectional segregation strategy. *ACS Applied Materials & Interfaces* **2018,** *10*, (29), 24947-24954.	2018	No	Yes (by the mainland team)	Yes

2017				**Qing, W.;** Shi, X.; Deng, Y.; Zhang, W.; **Wang, J.;** **Tang, C. Y.***	Robust superhydrophobic-superoleophilic polytetrafluoroethylene nanofibrous membrane for oil/water separation. *Journal of Membrane Science* **2017,** *540*, 354-361.	2018	No	Yes	Yes
2017				**Guo, H.;** **Yao, Z.;** **Yang, Z.**; **Ma, X.;** **Wang, J.;** **Tang, C. Y.***	A one-step rapid assembly of thin film coating using green coordination complexes for enhanced removal of trace organic contaminants by membranes. *Environmental Science & Technology* **2017,** *51*, (21), 12638-12643.	2018	No	Yes	Yes

9. Recognized international conference(s) in which paper(s) related to this research project was/were delivered *(Please attach a copy of each delivered paper. All listed papers must acknowledge RGC's funding support by quoting the specific grant reference.)*

Month/Year/ Place	Title	Conference Name	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*	Accessible from the institutional repository *(Yes or No)*
05/2019/Pittsburgh	One-Step Tailoring Surface Roughness and Surface Energy to Prepared Superhydrophobic Polyvinylidene Fluoride (PVDF) Membranes for Enhanced Membrane Distillation Performances	North American Membrane Society 2019 Annual Meeting	No	Yes	Yes	No (It is an oral presentation. No publication is involved).
08/2018/Lexington	Solvent-Thermal Induced Roughening: A Novel and Versatile Method to Prepare Superhydrophobic Membranes	North American Membrane Society 2018 Annual Meeting	2018	No	Yes	No (It is an oral presentation. No publication is involved).

10. Student(s) trained *(Please attach a copy of the title page of the thesis.)*

Name	Degree registered for	Date of registration	Date of thesis submission/ graduation
N.A.			

11. Other impact *(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, etc.)*

Patent
Qin Weihua, Shi Xiaonan, **Tang Chuyang**, Chinese Patent, ZL 201810045088.7, 提高聚合物薄膜表面粗糙度的方法及由其製備的薄膜

Awards
(1) **Tang Chuyang**, Inaugural HKU Innovator Award, 2020.
(2) **Guo Hao**, MIT Technology Review’s Innovator Under 35 for Asia Pacific, 2020.

12. Statistics on Research Outputs *(Please ensure the summary statistics below are consistent with the information presented in other parts of this report.)*

	Peer-reviewed journal publications	Conference papers	Scholarly books, monographs and chapters	Patents awarded	Other research outputs (Please specify)
No. of outputs arising directly from this research project [or conference]	13	2 conference presentations	N.A.	1	2 awards