Preparation of Highly Hydrophobic PVDF-HFP Membrane with Anti-Wettability Characteristic

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Abstract. Membrane gas-liquid separation technology has gained great interest in membrane desalination, distillation, and gas absorption attributed to its good operation flexibility, small footprint and high specific interfacial area. Membrane acts as the non-selective barrier between gas and liquid solvent by allowing the diffusion of gas molecules via pressure difference. Currently used membrane is susceptible to pore wetting at high operational pressure, transforming its non-wetted condition to partially wetted and wetted mode. Such condition introduces additional mass transfer resistance to gas molecules, leading to the poor removal flux. In order to alleviate the wetting tendency, membrane hydrophobicity needs to be enhanced. In this work, highly hydrophobic PVDF-HFP membrane of improved anti-wettability properties was synthesized via non-solvent induced phase separation. The effect of polymer concentration and coagulation medium on membrane wettability were studied. The results revealed that PVDF-HFP membrane of 10wt% polymer concentration presented high water contact angle of 100.4º. By changing water to ethanol as coagulation medium, membrane exhibited a symmetric nodular structure which enhanced water contact angle by 20.3% to 130.5º. To further improve membrane hydrophobicity, modified silica (MS) nanoparticles were used as surface modifier in coagulation bath. When the nanoparticles content increased from 0g to 2g, the water contact angle of the PVDF-HFP modified membrane increased significantly from 130.5° to 163.1°. As a result, the liquid entry pressure of the membranes increased gradually from 0.58bar to 3.38bar with MS incorporation. This disparity in membrane anti-wettability is due to the increase in surface roughness and reduction in surface energy. Additionally, the modified membrane at MS loading of 2g showed high porosity at 78%, which is adequate to provide increased mass transfer rate between gas and liquid solvent.

1. Introduction
Membrane gas-liquid separation technology has been widely employed in membrane desalination, distillation, and gas absorption to separate gas mixture using liquid solvent. This is attributed to its good operation flexibility, small footprint and high specific interfacial area [1]. In this process, the membrane is used as a barrier between gas and liquid phase by allowing the gas components to diffuse through the pores. This separation process requires a membrane with good hydrophobicity to ensure effective gas removal process in gas-filled pores [2]. Therefore, a great attention has been devoted to the hydrophobic membrane which has water contact angle higher than 90º.

The most attractive hydrophobic polymer is poly (vinylidene fluoride) (PVDF) attributed to its high chemical resistance, thermal stability and mechanical strength [3]. Nevertheless, PVDF membrane of insufficient hydrophobicity suffers from technical limitations impeding its application. Recently, PVDF based copolymer such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has emerged as a promising alternative due to its higher hydrophobicity [4].

In practice, membrane wetting is the main obstacle of membrane gas-liquid separation process. Pore wetting occurs if the operational pressure across the system exceeded the liquid entry pressure of the membrane, which resulted in partially or completely pore wetting. Wetting phenomenon distorted the membrane morphology and reduce the overall efficiency of the gas removal process. Hilal et al reported 13% of liquid-filled pores increase the membrane mass transfer resistance up to 90% [5].
Therefore, the membrane pore should be non-wetted to secure effective gas transport. By improving the membrane hydrophobicity, its LEP will be enhanced. This increases the allowable operational pressure difference in the system, consequently mitigates the wetting problem [6]. Attributed to its good wetting resistance, highly hydrophobic membrane allows for higher operational stability in gas removal process.

The wetting resistance of a solid surface is governed by its surface topography and surface chemistry [7]. Surface chemistry quantifies the disruption of intermolecular bonds on the surface meanwhile surface topography governs how these forces act upon the liquid. Therefore, membrane wetting resistance can be tuned by varying these two anti-wettability properties. In previous research, several attempts were studied to prepare highly hydrophobic membrane. Li et al employed the ethanol as the coagulation bath in preparing PVDF membrane. They discovered that membrane of improved hydrophobicity was synthesized with the use of soft precipitation bath [8]. The effect of membrane morphology on surface hydrophobicity was studied by Monical et al. They highlighted that symmetric membrane presented a higher hydrophobicity than the asymmetric membrane [9]. Ahmad and Ramli prepared the highly hydrophobic surface via soft coagulation bath system, and the contact angle of the membrane was as high as 127.2°C [10]. Meanwhile, Pramono et al reported that high polymer concentration lead to the formation of membrane with high surface hydrophobicity [11]. Other researchers also found that the use of hydrophobic nanoparticles in either dope solution or coagulation bath produced membrane with higher hydrophobicity [12-14]. These methods aim to generate highly hydrophobic surface by reducing the surface energy of a rough surface or roughening a surface with low surface energy.

In the present study, we aim to synthesis highly hydrophobic PVDF-HFP membrane of improved wetting resistance via non-solvent induced phase separation (NIPS). The studied parameters that affect the membrane hydrophobicity include the effect of polymer concentration, coagulation medium and additive concentration. The properties of the membranes including surface roughness, contact angle, pore size, porosity, morphology and liquid entry pressure was characterized.

2. Experimental

2.1. Materials

Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP, Mw 4.0×10^5gmol⁻¹, Mw/Mn = 3.08) pellets were supplied from Sigma Aldrich, USA as the polymer. N-methyl-2-pyrrolidone (NMP, 99.5%) was used as solvent in the polymer dope solution. Distilled water and ethanol (≥95%) were used as coagulation medium. Modified SiO₂ nanoparticles (MS) containing Si-O-Si bonds were kindly supplied by Wacker, Germany.

2.2. Fabrication of Flat Sheet PVDF-HFP Membrane

The experiment is divided into three phases in which to study the effect of polymer concentration, coagulation medium and additive concentration on membrane hydrophobicity. Polymer concentration was varied between 10, 15 and 20wt% in the first phase of experiment. Secondly, various coagulation medium (i.e. distilled water and ethanol (>95%) were used as coagulation medium. Modified SiO₂ nanoparticles (MS) containing Si-O-Si bonds were kindly supplied by Wacker, Germany.

The highly hydrophobic PVDF-HFP membranes were prepared via non-solvent induced phase-inversion process. PVDF-HFP pellets were dried at 70°C for 24 h to remove its moisture content. PVDF-HFP pellets were dissolved in NMP solvent and stir continuously for 24 h at 70°C. The dope polymer solution was degassed for 4 hr and left standing overnight. The degassed dope solution was cast on a glass plate of 200 casting gap at room temperature. After that, the cast film was immersed in coagulation bath for to undergo phase inversion. This is followed by immersion in distilled water to
remove the residual solvent and non-solvent additive. The resulting PVDF-HFP membrane was peeled off and dried in the room temperature for 48 h.

Table 1. Membrane composition and casting condition

| Sample | Polymer wt (%) | Thickness (μm) | Non-solvent | MS concentration (g/0.5L) |
|--------|----------------|---------------|-------------|---------------------------|
| M1-10  | 10             | 150           | Pure Distilled Water | -                         |
| M1-15  | 15             | 150           | Pure Distilled Water | -                         |
| M1-20  | 20             | 150           | Pure Distilled Water | -                         |
| M2-Wt  | 10             | 200           | Pure Distilled Water | -                         |
| M2-E   | 10             | 200           | Pure Ethanol     | -                         |
| M3-0.5 | 10             | 200           | Pure Ethanol     | 0.5                       |
| M3-1   | 10             | 200           | Pure Ethanol     | 1                         |
| M3-1.5 | 10             | 200           | Pure Ethanol     | 1.5                       |
| M3-2   | 10             | 200           | Pure Ethanol     | 2                         |

2.3. Membrane Characterization

2.3.1 Water contact angle.

The water contact angle was measured using a goniometer (Rame-Hart Instrument) to determine membrane hydrophobicity. Distilled water was dropped through a microsyringe onto the surface of the membrane at room temperature. The average value of each membrane was obtained from three measurements.

2.3.2 Porosity and pore size

The membrane porosity was measured by the dry-wet weight method. The membrane was first immersed in the isopropanol for 24h. The excess isopropanol on the membrane surface was wiped off before being weight. After that the membrane was dried overnight in oven to get dry weight. The porosity was calculated by the percentage of volume of isopropanol per volume of membrane [15].

The maximum pore size was determined using Coulter Porometer (Porolux 100 Porometer). The membrane was fully wetted by isopropanol and mounted on the sample chamber. The pressure of nitrogen gas was increased gradually. When the increased nitrogen gas reached a point that overcame the capillary flow of the fluid within the largest pores, the maximum pore size was found.

2.3.3 Liquid entry pressure (LEP)

The liquid entry pressure was measured to evaluate the wetting resistance of the membrane. LEP is defined as the pressure at which the liquid solvent penetrates the membrane. It is calculated using Eqn (1).

\[ P = \frac{4 \gamma \cos \theta}{d_p} \]  

Eqn (1)

Where \( d_p \) is the maximum pore size, \( \gamma \) is surface tension of liquid, \( \theta \) is the contact angle of membrane surface, and \( P \) is the liquid entry pressure.

2.3.4 Scanning electron microscopy

Scanning electron microscopy (Tabletop Microscope TM3030 Hitachi, Japan) was used to observe the surface and cross-sectional morphology of the resultant membrane. The cross section was obtained by
fracturing the membrane samples in liquid nitrogen. Energy dispersive X-ray spectroscopy (EDX) was performed to study the deposition of MS nanoparticles on the membrane surface.

2.3.5 Surface roughness
The surface roughness of the resultant membrane was obtained using a non-tapping mode atomic force microscopy (AFM). The measurement was carried out using a silicon cantilever over a 500 nm × 500 nm scan area at scanning rate of 1 Hz. The collected data were analyzed using NanoSope Analysis software.

3. Results and Discussions

3.1 Effect of polymer concentration
Polymer concentration is one of important factors that affected membrane hydrophobicity. Therefore, various polymer concentration (10, 15 and 20wt%) were studied to investigate the effect of polymer concentration on surface hydrophobicity. These membranes were labelled as M1-10, M1-15, and M1-20 according to the polymer concentration. Figure 1 shows the water contact angle for all resultant membranes. It is observed that water contact angle exhibited a declining trend with higher polymer concentration. When the polymer concentration increased from 10wt% to 20wt%, the water contact angle reduced from 100.4ºC to 79.4 ºC. A similar observation was found by Ahmad and Ramli [10]. This indicated that low polymer concentration has a positive impact on membrane surface hydrophobicity. As a result, a polymer concentration of 10wt% was suitably chosen to synthesis highly hydrophobic membrane.

![Fig. 1 Water contact angle of different polymer concentration](image)

3.2 Effect of coagulation medium
SEM micrographs of the water (M2-Wt) and ethanol induced membrane (M2-E) are demonstrated in Figure 2. When water was used as non-solvent, tight interconnected network was observed on membrane surface. The cross section of PVDF-HFP membrane exhibited an asymmetric structure, which composed of a finely porous skin layer supported by a sublayer of finger-like macrovoids [16]. By changing the water to ethanol, the membrane morphology is dominated by the polymer crystallization. As depicted in the cross-section morphology, the finger-like macrovoids was disappeared, instead, nodular structure was observed in the membrane due to the use of ethanol as soft non-solvent [8]. This resulted in the formation of monodisperse PVDF-HFP polymer spherulites. Similar morphology was observed by Monica et al. They highlighted that water induced membrane
exhibited an asymmetric structure and using ethanol as coagulation medium, the membrane presented spherical microparticles in the structure [9]. Attributed to the skinless structure, M2-E exhibited a higher surface roughness compared to the tight interconnected network in M2-Wt [17].

The disparity in morphology is attributed to the coagulation ability of coagulation medium. Compare to water, ethanol presents poorer coagulation ability due to lower kinetic coefficient and higher thermodynamic stability [18]. A great amount of ethanol is required to disrupt the polymer/solvent/non-solvent system and induce the precipitation. This delayed the liquid-liquid demixing and allowed the nucleation of polymer crystallization to dominate the precipitation situation. During phase-inversion process, the semi crystalline PVDF-HFP polymer grows gradually into spherical particles and interlinked via fibre-like connection. Subsequently, the crystallization-controlled process results in the nodular structure throughout the ethanol induced membrane. Meanwhile when water was used, liquid-liquid demixing induced instantaneous precipitation rate, and lead to the formation of macrovoids with finger-like structure.

The type of non-solvent in immersion precipitation process drastically alter the membrane hydrophobicity. Figure 3 demonstrated the water contact angles for the top surface of PVDF-HFP membranes. The water contact angle was 100.4ºC for the interconnected surface of water precipitated membrane. The use of ethanol significantly enhanced the water contact angle by 23% to 130.5º. According to SEM observation and water contact angle data, it can be concluded the surface hydrophobicity was enhanced by the skinless spherical structure. Such morphology provides a higher surface roughness due to the presence of polymer globules, hence increase the water contact angle. This kind of result was supported by Ooi et al [19]. They highlighted that soft precipitation bath induced the formation of symmetric structure which lead to higher surface roughness. This resulted in the enhancement of membrane hydrophobicity.

![SEM micrographs of PVDF-HFP membranes](image-url)
3.3 Effect of MS concentration

The surface and cross-sectional morphology of the modified membranes upon the incorporation of MS nanoparticles are shown in Figure 2. The nanoparticles are observed to be deposited between the polymer spherulites in modified membrane. As demonstrated in Figure 4, polymer globules were attached by some white clusters composed of MS nanoparticles. During the non-solvent/solvent exchange, the dispersed silica in coagulation bath tend to migrate on the polymer matrix, forming hierarchical clusters. As the MS loading increased, the surface of the modified membrane was gradually covered by a layer of MS nanoparticles. Hence, higher number of nanoparticles clusters was found on the surface of M3-2 compared to M3-0.5 membrane. This is due to enhanced embedment of modified-SiO$_2$ nanoparticles on the membrane surface as the nanoparticles loading increased. As depicted in cross-section morphology, the deposition of these nanoparticles was not smooth but form multilevel protrusions that are densely distributed on the surface. This resulted in bumpy surface composed of spherulites of different sizes.

The presence of MS nanoparticles was examined by EDX analysis. As depicted in Figure 4, the weight percentage of Si was increased with higher MS concentration. This shows enhanced additive attachment on the polymer spherical particles. In M1-0.5 to M1-2 membrane, the weight percentage of Si improved gradually from 10.73wt% to 29.83wt%. Besides, the F elemental composition on membrane surface decreased accordingly with higher MS loading. The significant decrease in weight percentage of F and the presence of Si on modified membrane confirmed the presence of MS nanoparticles on the membrane surface.
Table 2. EDX results on membrane surface

| Membrane | Composition (wt%) |
|-----------|------------------|
|           | C    | F    | O    | Si       |
| M2-Wt     | 37.96 | 60.3 | 1.74 | -        |
| M3-0.5    | 27.44 | 43.28| 18.55| 10.73    |
| M3-1      | 25.90 | 35.94| 22.43| 15.73    |
| M3-1.5    | 24.26 | 33.18| 22.82| 19.74    |
| M3-2      | 21.44 | 27.78| 26.95| 29.83    |

Figure 5 shows the wetting behavior of water molecules on the prepared PVDF-HFP membrane. The pristine membrane, M2-Wt exhibited the lowest contact angle of 100.4° compared to modified membranes. Upon the incorporation of MS nanoparticles, all modified membrane exhibited higher anti-wettability in term of water contact angle, which is desirable in membrane gas-liquid separation.
process to mitigate pore wetting. With increasing MS concentration from 0.5 to 2gL⁻¹, the water contact angle increases significantly from 145.8° up to 163.1°, showing superhydrophobic properties.

The enhancement of water contact angle was attributed by the surface roughening. This is consistent with the SEM morphology (Figure 2 and 4). Water precipitated membrane exhibited a tight interconnected structure on the surface, whereas the incorporation of nanoparticles induced the formation of multilevel protrusion on the modified membrane. According to Cassie-Baxter model, the rough surface created air pockets between protrusion and valley regions [20]. In this case, the hierarchical nanoparticles and air pockets form a composite surface with which the water droplet contacts, thereby reduced the direct contact area with the membrane surface. Additionally, the high hydrophobicity is contributed by the low surface free energy [21]. The surface free energy of the modified membranes was decreased by the presence of long chain non-polar bonds from MS nanoparticles. This reduced the interaction of membrane surface with other components. Both factors decrease the spreading of water droplet on the membrane surface. This leads to a high contact angle of 163°, rendering the surface superhydrophobic.

It has been reported that surface topography had a strong impact on the membrane hydrophobicity, whereby high surface roughness is required to achieve superhydrophobic surfaces [22]. The effect of MS nanoparticles on surface roughness was investigated. Figure 6 showed the surface topography and average roughness, $R_a$ of the resultant membranes. It was observed that the modified membrane, M3-2 exhibited higher surface roughness compared to the pristine membrane, M2-Wt. The surface roughness of the modified membrane was enhanced by 55.6% from 3.6nm to 8.1nm due to the deposition of silica nanoparticles. In the SEM images, the deposition of nanoparticles made the surface of modified membrane highly rough. This agreed well with the contact angle analysis, whereby an improvement in water contact angle was observed in modified membrane upon the incorporation of nanoparticles.
The porosity of the membrane was shown in Table 3. It was observed that the pristine membrane (M2-Wt) exhibited higher porosity than modified membrane (M3-2), which the porosities were 87.4% and 78.2% respectively. Membrane porosity maybe less affected by the MS loading as nanoparticles only formed a thin layer on the surface. The porosity of the modified membrane at 78% is still adequate to promote high mass transfer of gas molecules through the membrane pores [18]. Besides, the maximum pore size of M2-Wt is smaller than M3-2 membrane. Such disparity in porosity and pore size were caused by the significant change in membrane cross-section morphology, as depicted in Figure 2 and 4. Upon hydrophobic modification, the finger-like macrovoids morphology disappeared and followed by the formation of porous nodular structure [13]. This caused the reduction in membrane porosity and enhancement in pore size.

Table 3. Max pore size, LEP and porosity of the membranes

| Membrane sample | Max Pore size (μm) | LEP (bar) | Porosity (%) |
|-----------------|-------------------|-----------|--------------|
| M2-Wt           | 0.39              | 0.23      | 87.4         |
| M3-2            | 0.80              | 3.38      | 78.2         |

As aforementioned, one of the critical membrane characteristics in membrane gas-liquid separation process is liquid entry pressure. As can be seen in Table 1, the addition of MS nanoparticles raised the LEP values from 0.23 bar for pristine membrane (M2-Wt) to 3.38 bar for M-2 membrane. This is due to the enhancement of the water contact angle. An increase of 63° in water contact angle was observed in membrane M3-2 due to the enhancement in surface roughness and reduction of surface free energy. It is expected that the membrane with the inclusion of nanoparticles will mitigate the wetting problem at higher operational pressure.

Conclusion
By using the polymer concentration of 10%, the surface hydrophobicity of the membrane achieved high contact angle of 100.4°. To improve the membrane hydrophobicity, ethanol was used as coagulation medium instead of water. As a result, the water contact angle of the membrane was enhanced to 130.5°. The superhydrophobicity was achieved via surface modification by modified silica nanoparticles. With the use of MS nanoparticles, the surface roughness of the membrane was increased compared to pristine membrane, M2-Wt. Subsequently, the water contact angle and liquid entry pressure of the membranes were enhanced from 100.4° to 163.1° and 0.23 bar to 3.38 bar respectively. Therefore, the modified membranes are expected to reduce the tendency of pore wetting at high operational pressure. The porosity of the membrane was slightly reduced upon the use of nanoparticles in ethanol bath. Nevertheless, the porosity of modified membrane is still adequate to promote high mass transfer in gas-liquid separation. The synthesized highly hydrophobic PVDF-HFP membrane of great potential to be used in membrane gas-liquid separation application for improved water-repellency.
References

[1] B. Shimekit and H. Mukhtar, “Natural gas purification technologies-major advances for CO2 separation and future directions,” in Advances in natural gas technology, ed: InTech, 2012.

[2] H. Tang, Y. Zhang, F. Wang, H. Zhang, and Y. Guo, “Long-term stability of polytetrafluoroethylene (PTFE) hollow fiber membranes for CO2 capture,” Energy & Fuels, vol. 30, pp. 492-503, 2015.

[3] J. E. Efome, M. Baghbanzadeh, D. Rana, T. Matsuura, and C. Q. Lan, “Effects of superhydrophobic SiO2 nanoparticles on the performance of PVDF flat sheet membranes for vacuum membrane distillation,” Desalination, vol. 373, pp. 47-57, 2015/10/01/ 2015.

[4] L. Zheng, J. Wang, Y. Wei, Y. Zhang, K. Li, and Z. Wu, “Interconnected PVDF-CTFE hydrophobic membranes for MD desalination: effect of PEGs on phase inversion process,” RSC Advances, vol. 6, pp. 20926-20937, 2016.

[5] N. Hilal, A. F. Ismail, and C. Wright, Membrane fabrication: CRC Press, 2015.

[6] D. Hou, G. Dai, H. Fan, J. Wang, C. Zhao, and H. Huang, “Effects of calcium carbonate nanoparticles on the properties of PVDF/nonwoven fabric flat-sheet composite membranes for direct contact membrane distillation,” Desalination, vol. 347, pp. 25-33, 2014.

[7] G. B. Darband, M. Alishahraei, S. Khorsand, S. Sokhanvar, and A. Kaboli, “Science and Engineering of Superhydrophobic Surfaces: Review of Corrosion Resistance, Chemical and Mechanical Stability,” Arabian Journal of Chemistry, 2018.

[8] Q. Li, Z.-L. Xu, and M. Liu, “Preparation and characterization of PVDF microporous membrane with highly hydrophobic surface,” Polymers for Advanced Technologies, vol. 22, pp. 520-531, 2011.

[9] T. Mónica Beatrix, P. Patricila, M. Marcos, D. Jocelei, and Z. Mara, “Ref 26 Effect of non-solvents used in the coagulation bath on morphology of PVDF membranes,” Materials Research, vol. 15, pp. 884-890, 2012.

[10] A. L. Ahmad and W. K. W. Ramli, “Hydrophobic PVDF membrane via two-stage soft coagulation bath system for Membrane Gas Absorption of CO2,” Separation and Purification Technology, vol. 103, pp. 230-240, 2013/01/15/ 2013.

[11] E. Pramono, A. Simamora, C. Radiman, and D. Wahyuningrum, “Effects of PVDF concentration on the properties of PVDF membranes,” in IOP Conference Series: Earth and Environmental Science, 2017, p. 012027.

[12] X. Wu, B. Zhao, L. Wang, Z. Zhang, J. Li, X. He, et al., “Superhydrophobic PVDF membrane induced by hydrophobic SiO2 nanoparticles and its use for CO2 absorption,” Separation and Purification Technology, vol. 190, pp. 108-116, 2018/01/08/ 2018.

[13] M. Rahbari-Sisakht, A. Ismail, D. Rana, and T. Matsuura, “A novel surface modified polyvinylidene fluoride hollow fiber membrane contactor for CO2 absorption,” Journal of membrane science, vol. 415, pp. 221-228, 2012.

[14] T. Li, P. Yu, and Y. Luo, “Preparation and properties of hydrophobic poly(vinylidene fluoride)-SiO 2 mixed matrix membranes for dissolved oxygen removal from water,” Journal of Applied Polymer Science, vol. 131, pp. n/a-n/a, 2014.

[15] S. Munirasu, F. Banat, A. A. Durran, and M. A. Haija, “Intrinsically superhydrophobic PVDF membrane by phase inversion for membrane distillation,” Desalination, vol. 417, pp. 77-86, 2017/09/01/ 2017.

[16] L. P. Cheng, D. J. Lin, C. H. Shih, A. H. Dwan, and C. C. Gryte, “PVDF membrane formation by diffusion-induced phase separation-morphology prediction based on phase behavior and mass transfer modeling,” Journal of Polymer Science Part B: Polymer Physics, vol. 37, pp. 2079-2092, 1999.

[17] N. Hamzah and C. P. Leo, “Fouling prevention in the membrane distillation of phenolic-rich solution using superhydrophobic PVDF membrane incorporated with TiO2 nanoparticles,” Separation and Purification Technology, vol. 167, pp. 79-87, 2016/07/14/ 2016.

[18] P. Sukitpaneenit and T.-S. Chung, “Molecular elucidation of morphology and mechanical properties of PVDF hollow fiber membranes from aspects of phase inversion, crystallization and rheology,” Journal of Membrane Science, vol. 340, pp. 192-205, 2009.
[19] B. S. Ooi, N. S. M. Yatim, A. L. Ahmad, and S. O. Lai, "Preparation of polyvinylidene fluoride membrane via dual coagulation bath system and its wettability study," *Journal of Applied Polymer Science*, vol. 124, pp. E225-E232, 2012.

[20] N. J. Shirtcliffe, G. McHale, S. Atherton, and M. I. Newton, "An introduction to superhydrophobicity," *Advances in colloid and interface science*, vol. 161, pp. 124-138, 2010.

[21] S. Mosadegh-Sedghi, D. Rodrigue, J. Brisson, and M. C. Iliuta, "Wetting phenomenon in membrane contactors – Causes and prevention," *Journal of Membrane Science*, vol. 452, pp. 332-353, 2014/02/15/ 2014.

[22] A. Razmjou, E. Arifin, G. Dong, J. Mansouri, and V. Chen, "Superhydrophobic modification of TiO2 nanocomposite PVDF membranes for applications in membrane distillation," *Journal of membrane science*, vol. 415, pp. 850-863, 2012.

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