Fabrication of bioinspired composite nanofiber membranes with robust superhydrophobicity for direct contact membrane distillation

Fane, Anthony Gordon; Liao, Yuan; Wang, Rong

2014

Liao, Y., Wang, R., & Fane, A. G. (2014). Fabrication of bioinspired composite nanofiber membranes with robust superhydrophobicity for direct contact membrane distillation. *Environmental science & technology*, 48(11), 6335-6341.

<https://hdl.handle.net/10356/105894>

<https://doi.org/10.1021/es405795s>

© 2014 American Chemical Society. This is the author created version of a work that has been peer reviewed and accepted for publication by *Environmental Science & Technology*. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1021/es405795s>].

Downloaded on 26 Apr 2023 18:03:31 SGT

Fabrication of bioinspired composite nanofiber membranes with robust superhydrophobicity for direct contact membrane distillation

Yuan Liao^{†,‡}, Rong Wang^{†,‡}, Anthony G. Fane^{†,‡}*

[†]School of Civil and Environmental Engineering,
Nanyang Technological University, 639798 Singapore

[‡]Singapore Membrane Technology Centre,
Nanyang Environment and Water Research Institute,
Nanyang Technological University, 637141 Singapore

*corresponding author, Email: rwang@ntu.edu.sg

ABSTRACT

The practical application of membrane distillation (MD) for water purification is hindered by the absence of desirable membranes that can fulfill the special requirements of MD process. Compared to the membranes fabricated by other methods, nanofiber membranes produced by electrospinning are of great interest due to their high porosity, low tortuosity, large surface pore size and high surface hydrophobicity. However, the stable performance of the nanofiber membranes in MD process is still unsatisfactory. Inspired by the unique structure of lotus leaf, this study aimed to develop a strategy to construct superhydrophobic composite nanofiber membranes with robust superhydrophobicity and high porosity suitable for use in MD. The newly developed membrane consists of a superhydrophobic silica-PVDF composite selective skin formed on polyvinylidene fluoride (PVDF) porous nanofiber scaffold via electrospinning. This fabrication method could be easily scaled up due to its simple preparing procedures. The effects of silica diameter and concentration on membrane contact angle, sliding angle and MD performance were investigated thoroughly. For the first time, the direct contact membrane distillation (DCMD) tests demonstrate that the newly developed membranes are able to present stable high performance over 50 hours of testing time, and the superhydrophobic selective layer exhibits excellent durability in ultrasonic treatment and continuous DCMD test. It is believed that this novel design strategy has great potential for MD membrane fabrication.

TOC art

INTRODUCTION

Clean water is essential to healthy ecosystem and sustainable socio-economic development. The increasing pressure on freshwater resources calls for effective and novel approaches to produce high-quality water. Among various technologies, membrane distillation (MD) is an emerging process that can utilize low-grade or waste heat to generate high-quality water from impaired water with high recovery (100% in theory).¹ MD is gaining attention as a low Greenhouse gas (GHG) option for water purification. In its simplest configuration, direct contact membrane distillation (DCMD) involves the transportation of water vapor from a hot feed stream through a hydrophobic micro-porous membrane and the condensation of the water vapor into a cool permeate, where the driving force is the vapor pressure difference across the membrane.² The DCMD is schematically shown in Figure S1 (Supporting Information).

In the DCMD process, the hydrophobic membrane serves as the barrier between the two liquid phases of feed and permeates and its properties determine the system performance. In order to deliver high vapour permeability and ensure high water quality, the membrane should possess appropriate pore sizes and high porosity.³ To avoid membrane pore wetting, at least one layer of the MD membrane should be hydrophobic or preferably superhydrophobic.⁴ Moreover, the MD membrane should be physically robust, exhibit excellent thermal stability and maintain a stable performance in long-term usage. However, specially designed MD membranes are not commercially available and most membranes used were initially designed for micro-filtration. Such membranes are suboptimal for MD applications and suffer from progressive membrane wetting in the MD process. Therefore, the development of improved membranes that can fulfill the unique requirements of MD is imperative to facilitate practical applications of the MD process. **So far, hydrophobic flat-sheet microporous membranes made from**

modified polyvinylidene fluoride (PVDF) were prepared by phase inversion process for MD.⁵ The effects of hydrophobic additives on resultant hollow fiber membranes performance in MD process were investigated.^{6, 7} Additionally, surface modification has been carried out to improve hollow fiber membrane properties.⁸ It is well-recognized that due to the high porosity, low tortuosity and interconnected structure, nanofiber membranes are highly attractive to be used as MD membranes.⁹⁻¹²

Nature provides many inspirations for novel synthetic materials. The most well-known example of superhydrophobic natural plants is the lotus leaf. The well-documented “lotus effect” reports that water droplets on a lotus leaf are spherical in shape and able to roll off easily, which is caused by the uniform protrusions and valleys on the leaf surface.¹³ Detailed field emission scanning electron microscopy (FESEM) images of the lotus leaf (inserted pictures in **Figure 1**) reveal that hydrophobic wax-like materials are decorated on the protrusions and valleys as the secondary structure. Superhydrophobic glass membranes with integrated arrays of nanospiked microchannels were prepared by complicated glass fiber drawing, dissolving template materials and chemical etching.¹⁴ However, the resultant membrane exhibited a low mass flux of 3.3 kg/m² per hour when the feed was a 5 wt% salt solution at 65 °C. On the other hand, the superhydrophobic membrane can mitigate fouling by reducing water-membrane contact area.

Inspired by the lotus leaf structure, in our current work, a novel nanocomposite MD membrane has been designed as shown in **Figure 1**. A scaffold-like PVDF nanofiber membrane made by electrospinning, with high porosity and low tortuosity and an adjustable thickness, is used as a mechanical support. A silica-PVDF composite selective layer, which has an extremely high water contact angle (>150°) and water repelling properties, is formed on the top of the support via the same electrospinning technique. It

is expected that the silica-PVDF composite layer has a similar hierarchical structure to the lotus leaf, and is able to form air pockets or water vapour pockets on the membrane surface during the MD process, leading to the lowest contact area between water and the membrane. The unstable contact line points can force the water droplets to roll off the membrane surface spontaneously. Furthermore, the effects of the diameter and concentration of silica on water contact angle, water sliding angle of resultant membranes were studied. The durability of the superhydrophobic selective layer was tested in ultrasonic treatment. Finally, the DCMD tests were performed to demonstrate the stable high performance of the newly developed membranes in long-term MD operations. To the best of our knowledge, it is the first time to propose this easy and convenient approach to fabricate dual-layer superhydrophobic microporous membranes by electrospinning for DCMD process. Due to the unique architecture, the membranes are expected to possess better performance than other superhydrophobic membranes mentioned previously.

MATERIALS AND METHODS

Materials

Commercial polymer polyvinylidene fluoride (PVDF) Kynar HSV 900 was purchased from Arkema Inc., Singapore and was dried at 50 °C under vacuum before use. N, N-Dimethylformamide (DMF) as solvent and lithium chloride (LiCl) as additives in polymer dopes were provided by Merck, Singapore. Isopropyl alcohol (IPA) with analytical grade was obtained from VWR Co. Ltd, Singapore. Silica with an average aggregate particle size between 0.2 to 0.3 μm and in spherical shapes with a particle size of 5 – 15 nm were purchased from Sigma-Aldrich, Singapore. For the silica surface modification, α , ω -triethoxysilane terminated perfluoropolyether ((EtO)₃Si-PFPE-Si(OEt)₃) with an average molecular weight between 1750 to 1950 was obtained from Solvay Solexis under the trade name Fluorolink® S10 and was coded

as FS10. Tetraethoxysilane (TEOS) (Merck, Singapore) was used as an additive to enhance the modification efficiency. N-hexane also provided by Merck in Singapore was used as a dispersive solvent for modification. All reagents were used as received. Water was purified with a Milli-Q system (Millipore Co. Singapore). Commercial PVDF membranes, Durapore® Membrane filter, were obtained from Millipore, Singapore to compare with the composite PVDF membranes.

Silica modification and dope preparation

Briefly, a desired amount of silica nanoparticles was stirred rapidly over night in N-hexane solution in which FS10 and TEOS with a mass ratio of 3:2 was added. The total concentration of FS10 and TEOS was 5 wt%. The modified SiO₂ nanoparticles were then separated by centrifugation and annealed in a vacuum oven at 100 °C for 1 hour. The resultant white powder was stored over night in a vacuum oven at 50 °C prior to further experiments and characterization.

PVDF precursor solutions for the superhydrophobic layer were prepared by initially dissolving 5 wt.% PVDF HSV 900 in DMF. Then modified SiO₂ with different diameters were dispersed in prepared 5 wt% PVDF solution by stirring rapidly at room temperature. The mass ratio of modified SiO₂ particles/PVDF was fixed at 2:1 to guarantee the superhydrophobic effects.¹⁵

Electrospinning of PVDF nanofiber membranes and composite superhydrophobic membranes

The PVDF nanofiber membranes and superhydrophobic composite silica-PVDF membranes were prepared via an electrospinning setup as reported in our previous work.¹¹ As shown in Table S1, the PVDF nanofiber support was fabricated by a 8 wt% PVDF dope. After spinning the porous substrate, the superhydrophobic surface layers were electrospun using two modified silica-blended PVDF dopes. One

dope was the mixture of PVDF and small silica particles with diameters of 5-10 nm while the another was prepared by dispersing larger hydrophobic SiO₂ particles with aggregate diameters of 0.2-0.3 μm in a 5 wt% PVDF dope. As the purpose was to investigate the effects of the superhydrophobic layer precisely on the membrane properties, all the composite membranes had the same substrate layer. The characterizations of the resultant membranes are illustrated in Supporting Information.

MD performance tests

The MD performance was tested in a DCMD setup with an effective membrane area of 38 cm². The DCMD setup has been detailed in our previous work.¹¹ Both the feed and permeate solutions were cycled through the flat-sheet membrane cell. On the hot feed side, the liquid was a 3.5 wt% sodium chloride aqueous solution, which was heated to 333 K and circulated with a flow rate of 0.8 L·min⁻¹. On the cold permeate side, DI water with conductivity below 5 $\mu\text{S}/\text{cm}$ was cooled down to 293 K and circled by a peristaltic pump at the same flow rate. The permeate flux was collected in an overflow tank located on a digital balance.

RESULTS AND DISCUSSION

In order to prepare a robust superhydrophobic surface, the silica nano-particles were first modified by perfluoropolyether (FS10), which made them hydrophobic to easily disperse in the second PVDF dope solution and able to stick to the PVDF ‘islands’ on the substrate, allowing the top surface to be more durable.¹⁵ The chemical structure of the modifying agent, FS10, and the possible modification reaction pathway on the SiO₂ surface are given in Figure S2, which are demonstrated by XPS analysis. To examine the surface enrichment of fluorocarbon chains on the modified silica, an XPS analysis was carried out on unmodified and modified SiO₂ surfaces, as shown in Figure S3. It confirmed that the

silica surface was successfully covered by the FS10, which shifted the hydrophilic silica nano-particles with OH groups to hydrophobic fluorinated nano-particles.

To further demonstrate that the superhydrophobic membrane surface contains modified silica particles and the modified silica was covered and protected by thin PVDF layers, independent evaluations of the surface characteristics of the original PVDF nanofiber and silica-PVDF composite membranes were conducted by XPS. As shown in **Figure 2A**, the C 1s core-level spectrum of the PVDF nanofiber membrane can be simply curve-fitted with two peak components, one at a binding energy (BE) of 285.0 eV for the carbon bonded to hydrogen (CH_x) and the other at BE of 290 eV for a single carbon bonded to fluorine (CF_2),¹⁶ which is typical of the C1s core level spectrum for PVDF. As shown in **Figure 2B**, small amounts of hydrocarbon and fluoride carbon were also present on FS10-SiO₂ due to the chemical structure of FS10, and the prominent CF envelope can be fitted with two peaks that correspond to $\text{O-CF}_2\text{-O}$ and $\text{O-CF}_2\text{-O}$ at 294.9 eV and 293.5 eV, respectively.¹⁷ Beside these peaks, there are two other peaks that are attributed to the $\text{O-CH}_2\text{-C}$ (286.6 eV) and -CO-N- (287.9 eV) chemical bonds of the FS10 structure.¹⁸ According to the parameters determined from the curve fitting of the superhydrophobic silica-PVDF composite membrane (**Figure 2C**), the C1s envelope identifies the primary presence of $\text{-CH}_2\text{-}$ and $\text{-CF}_2\text{-}$, which means the surface layer (within 10 nm) was mainly bound and covered by PVDF material.

Optical photographs of the PVDF nanofiber membrane which was fabricated by 8 wt% PVDF dissolved in N, N-Dimethylformamide (DMF) and the superhydrophobic silica-PVDF composite membrane are shown in **Figures 3A** and **3B**, respectively. As shown in the FESEM image inserted in **Figure 3A**, the PVDF nanofiber membrane surface presents a continuous arrangement of nanofibers with an average

diameter of 170 nm. The nanofiber PVDF membrane possesses a contact angle of 142.8° , which is much higher than other PVDF membranes prepared by non-solvent induced phase separation.¹⁹ However, the PVDF nanofiber membrane also shows a high contact angle hysteresis. For example, it is observed that a water droplet cannot roll off from its surface even when the membrane is turned upside down as shown in small inserted pictures in **Figure 3C**. This is the so-called petal effect or Cassie impregnating wetting state.²⁰ Water droplets tend to penetrate into the larger-scaled grooves between the nanofibers and remain spherical above the nanofiber membrane. It is evident that the water sealed in the micro-sized grooves would assist water droplets in adhering to the membrane surface due to the surface tension force.

On the other hand, after the modified SiO₂-PVDF blended dope (10 wt% SiO₂ and 5 wt% PVDF were mixed in DMF solvent homogeneously) was sprayed via electrospinning onto the nanofiber membrane surface, the nanofibers and nano-beads structure could be formed on the composite membrane surface as shown in **Figure 3B**. The nanofiber diameter was around 90 nm. The thinner diameter of the modified PVDF nanofibers was probably due to the lower polymer concentration used compared with the pure PVDF dope used for preparing the substrate.¹¹ The water contact angle of the composite membrane is 156.3° . Additionally, the composite membranes possess excellent water repellence property as shown in **Figure 3D**. Similar to lotus leaf, the composite silica-PVDF membranes have a microstructure consisting of modified silica-PVDF mixed islands and a nanostructure comprising PVDF-bound silica nanoparticles on the islands surface. This hierarchical structure prevents water from intruding into the microstructural spaces. The triple contact lines between the solid and liquid or the solid and air on the randomly rough surface are expected to be contorted and unstable, which makes the water droplets easily moved.¹³

The deposition of modified silica-PVDF mixture on the PVDF nanofiber support by electrospinning is the critical step to shift the membrane from hydrophobic to superhydrophobic. The effects of the modified silica particle sizes which are 0.2- 0.3 μm and 10 - 15 nm, respectively, and spinning layers on water contact angle and sliding contact angle were investigated as shown in **Figure 4**. The technique for measuring sliding contact angle is illustrated in Figure S4. It can be seen from **Figure 4** that the diameter of the modified silica particles has no obvious impact on water contact and sliding angles of as-prepared membranes. After spinning 3 layers of the composite dope, the membranes have contact angles over 150° and exhibit water repellence properties due to the formation of both microstructures and secondary nanostructures. With an increase in spinning layer number, the contact angle of the composite membranes increased progressively to a plateau and the sliding contact angle decreased slightly. This is probably due to the enhancement of hierarchical structures. Furthermore, the water sliding angle difference between the PVDF nanofiber membrane and the composite membrane is pronounced. The PVDF nanofiber membrane shows a strong adhesive force for water droplets so that they cannot move, while the composite membrane has a low sliding angel less than 20° . It is believed that the micro- and nano-roughness increased the presence of air pockets on the composite membrane surface significantly, which could effectively trap air between the liquid and solid surface, preventing the liquid from penetrating into the surface cavities. Thus the build-up of a discrete contact between the liquid and the solid leads to the drastic reduction of sliding contact angle.²¹ Since the composite membranes with 9 superhydrophobic layers have the highest contact angle and the lowest sliding angle, the S-PVDF and L-PVDF, which refer to the membranes with small and large modified silica nanoparticles, respectively, were chosen for further study.

Prior to using the superhydrophobic membranes for MD tests, their durability was examined by ultrasonic treatment. As shown in Figure 5S, compared with the L-PVDF membrane, the water contact angle of S-PVDF membrane decreased slightly after ultrasonic treatment. The possible reason is that a small amount of the modified silica particles on the S-PVDF membrane might be removed during the ultrasonic treatment, while the big particles on the L-PVDF membrane have better inter-tangled force with the polymer chains, making them more stable on the membrane surface. Nevertheless, both the S-PVDF and L-PVDF membranes still possess high contact angles above 150° and excellent water repellent properties after ultrasonic treatment for 30 minutes. Under FESEM, the surface morphologies of the S-PVDF and L-PVDF membranes also show no obvious difference before and after 30 min ultrasonic-treatment.

The MD performances of the PVDF nanofiber membrane, the composite membranes S-PVDF, L-PVDF and a commercial PVDF membrane (Durapore® Membrane filter, Millipore, Singapore) were tested in the DCMD configuration. As shown in **Table 1**, the PVDF nanofiber membrane has 142.8° water contact angle, $0.68\ \mu\text{m}$ surface mean pore size and $1.27\ \mu\text{m}$ max pore size. The composite membranes S-PVDF and L-PVDF have higher contact angles of 156.3° and 153.9° , respectively, with similar surface pore sizes that are much larger than the commercial Millipore hydrophobic membranes. In addition, the three electro-spun membranes exhibit higher porosity, around 83%, than the commercial membrane. For a fair comparison, all the membranes used in the DCMD tests have a similar thickness between 100 to $130\ \mu\text{m}$. Due to the surface superhydrophobicity, the S-PVDF and L-PVDF membranes present a higher LEP_w (liquid enter pressure) than the PVDF nanofiber membrane. The commercial PVDF has the highest LEP_w due to its smaller pore size. Other membrane properties are also included in **Table 1**.

The MD tests were performed using a 3.5 wt% NaCl solution as the feed solution under a temperature of 60°C and the permeate side was set at 20°C. As shown in **Figure 5**, the permeate flux of the composite membranes S-PVDF and L-PVDF were 18.1 kg/m²hr and 18.9 kg/m²hr, respectively, while the PVDF nanofiber membrane had a flux around 12.3 kg/m²hr and the commercial PVDF flux was about 10 kg/m²hr. The composite membranes showed a stable performance over 50 hours of testing time and produced high quality water with conductivity below 5.0 µS/cm. However, the conductivity of the product water from the PVDF nanofiber membrane generally increased during 45 hours usage. The more stable performances of the composite membranes are attributed to their greater hydrophobicity and the better water repellence of the membrane surface. There are several possible explanations for the higher water flux of the composite membranes compared with the PVDF nanofiber membrane. Firstly, when the hot salt solution on the feed side was flowing across the fresh nanofiber membrane surface during the test, water droplets might have gradually entered into the nanofiber sheet and accumulated between the nanofiber layers due to their loose overlap, which would reduce the temperature difference between the feed and permeation sides and thus decrease water flux significantly.¹¹ The FESEM images in **Figures 6A and 6B** illustrate that a large gap appeared between the nanofiber layers due to the feed water accumulation, though no obvious feature changes can be observed on the tested membrane surface. Secondly, the superhydrophobic composite PVDF membranes have higher effective surface porosity which offers more boundaries for phase transition from water in the aqueous salt solution to vapour than the nanofiber membrane. As depicted in **Figure 7**, the meniscus at the membrane surface represents the effective liquid evaporation area. Compared with the nanofiber membrane in which the feed solution is entrapped between nanofibers due to the Petal effect, the superhydrophobic composite membranes have larger effective liquid evaporation areas because of the Lotus effect. As described previously, the

hierarchical structure with increased roughness on a superhydrophobic surface would provide numerous orifices to trap water vapour inside during the MD process, and this tends to reduce the contact area between the liquid and solid but increase the contact areas between the liquid and vapour. This type of structure not only provides the surface with superhydrophobic and self-cleaning properties, it also provides more effective liquid areas to evaporate the water vapour and enhance the permeation flux in the MD process. Additionally, the superhydrophobic composite membranes have thin regions of increased vapour and air entrapment, which could lower the effective thermal conductivity of the membranes and thus reduce conductive heat losses and provide more driving force for evaporative transfer in the MD process. In contrast, as shown in **Figure 5D**, the flux of commercial PVDF was around 10.0 kg/m²hr. The newly developed superhydrophobic PVDF membranes are very competitive compared with the commercial flat-sheet PVDF membrane.

The stability of composite PVDF membranes in DCMD process was also investigated. According to the FESEM images shown in **Figure 6**, after being scoured by salt water for over 50 hours, the superhydrophobic S-PVDF and L-PVDF membranes still have the similar surface morphology as previously. The modified silica-blended PVDF beads could be observed on the composite membrane surface. Additionally, the S-PVDF and L-PVDF membranes still possess high water contact angle above 150° and excellent water repellence, while the surface of the PVDF nanofiber membrane maintains a strong adhesive force with water droplets, which demonstrates that the electrospun membranes are durable in the DCMD application. To further improve membrane performance in DCMD process, the optimization of membrane thickness could be carried out in future research.²² Moreover, the stability of electrospun membrane in DCMD configuration could be improved by constructing a thin spider-web-like nano-nets layer on the membrane surface which has ultrafine nanofibers and small pore sizes.²³

ASSOCIATED CONTENT

SUPPORTING INFORMATION

Characterizations of PVDF nanofiber and composite membranes; DCMD process (Figure S1); mechanisms of modification reaction on silica nanoparticles (Figure S2); surface elemental analysis of silica nanoparticles before and after modification (Figure S3); water sliding angle measurement (Figure S4); stability of superhydrophobic layers after ultrasonic treatment (Figure S5); electrospinning conditions of PVDF nanofiber membrane and silica-PVDF composite membranes (Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

Email: rwang@ntu.edu.sg Tel: (65) 6790-5327 Fax: (65) 6515-5981

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This research grant is supported by the Singapore National Research Foundation under its Environmental & Water Technologies Strategic Research Programme and administered by the Environment & Water Industry Programme Office (EWI) of the PUB (EWI RFP 0901-IRIS-02-03). The first author is supported by the National Research Foundation Singapore under its National Research Foundation (NRF) Environmental and Water Technologies (EWT) PhD Scholarship Programme and administered by the Environment and Water Industry Programme Office (EWI). We also acknowledge funding support from the Singapore Economic Development Board to the Singapore Membrane

Technology Centre. Finally the authors gratefully acknowledge the help from Ms. Lau Zhihui from the Civil and Environmental Engineering School, Nanyang Technological University.

References

- (1) Pal, P.; Manna, A. Removal of arsenic from contaminated groundwater by solar-driven membrane distillation using three different commercial membranes. *Water Res.* **2010**, *44* (19), 5750-5760.
- (2) Yang, X.; Wang, R.; Fane, A. G. Novel designs for improving the performance of hollow fiber membrane distillation modules. *J. Membr. Sci.* **2011**, *384* (1–2), 52-62.
- (3) Mohamed, K. Membranes and theoretical modeling of membrane distillation: A review. *Advances in Colloid and Interface Science* **2011**, *164* (1-2), 56-88.
- (4) Wang, P.; Chung, T.-S. A New-Generation Asymmetric Multi-Bore Hollow Fiber Membrane for Sustainable Water Production via Vacuum Membrane Distillation. *Environ. Sci. Technol.* **2013**, *47* (12), 6272-6278.
- (5) Feng, C.; Shi, B.; Li, G.; Wu, Y. Preparation and properties of microporous membrane from poly(vinylidene fluoride-co-tetrafluoroethylene) (F2.4) for membrane distillation. *J. Membr. Sci.* **2004**, *237* (1–2), 15-24.
- (6) Teoh, M. M.; Chung, T.-S. Membrane distillation with hydrophobic macrovoid-free PVDF–PTFE hollow fiber membranes. *Sep. Purif. Technol.* **2009**, *66* (2), 229-236.
- (7) Edwie, F.; Teoh, M. M.; Chung, T.-S. Effects of additives on dual-layer hydrophobic–hydrophilic PVDF hollow fiber membranes for membrane distillation and continuous performance. *Chem. Eng. Sci.* **2012**, *68* (1), 567-578.
- (8) Yang, X.; Wang, R.; Shi, L.; Fane, A. G.; Debowski, M. Performance improvement of PVDF hollow fiber-based membrane distillation process. *J. Membr. Sci.* **2011**, *369* (1–2), 437-447.
- (9) Liao, Y.; Wang, R.; Fane, A. G. Engineering superhydrophobic surface on poly(vinylidene fluoride) nanofiber membranes for direct contact membrane distillation. *J. Membr. Sci.* **2013**, *440* (0), 77-87.

- (10) Prince, J. A.; Singh, G.; Rana, D.; Matsuura, T.; Anbharasi, V.; Shanmugasundaram, T. S. Preparation and characterization of highly hydrophobic poly(vinylidene fluoride) – Clay nanocomposite nanofiber membranes (PVDF–clay NNMs) for desalination using direct contact membrane distillation. *Journal of Membrane Science* **2012**, 397–398 (0), 80-86.
- (11) Liao, Y.; Wang, R.; Tian, M.; Qiu, C.; Fane, A. G. Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation. *J. Membr. Sci.* **2013**, 425–426 (0), 30-39.
- (12) Feng, C.; Khulbe, K. C.; Matsuura, T.; Gopal, R.; Kaur, S.; Ramakrishna, S.; Khayet, M. Production of drinking water from saline water by air-gap membrane distillation using polyvinylidene fluoride nanofiber membrane. *J. Membr. Sci.* **2008**, 311 (1–2), 1-6.
- (13) Bhushan, B.; Jung, Y. C. Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction. *Prog. Mater Sci.* **2011**, 56 (1), 1-108.
- (14) Ma, Z.; Hong, Y.; Ma, L.; Su, M. Superhydrophobic Membranes with Ordered Arrays of Nanospiked Microchannels for Water Desalination. *Langmuir* **2009**, 25 (10), 5446-5450.
- (15) Wang, S.; Li, Y.; Fei, X.; Sun, M.; Zhang, C.; Li, Y.; Yang, Q.; Hong, X. Preparation of a durable superhydrophobic membrane by electrospinning poly (vinylidene fluoride) (PVDF) mixed with epoxy–siloxane modified SiO₂ nanoparticles: A possible route to superhydrophobic surfaces with low water sliding angle and high water contact angle. *J. Colloid Interface Sci.* **2011**, 359 (2), 380-388.
- (16) Moussaif, N.; Pagnouille, C.; Riga, J.; Jérôme, R. XPS analysis of the PC/PVDF interface modified by PMMA. Location of the PMMA at the interface. *Polymer* **2000**, 41 (9), 3391-3394.

- (17) Toselli, M.; Gardella, J. A.; Messori, M.; Hawkrigde, A. M.; Pilati, F.; Tonelli, C. Surface chemical analysis of poly(ϵ -caprolactone)–perfluoropolyether–poly(ϵ -caprolactone) triblock copolymers by X-ray photoelectron spectroscopy. *Polym. Int.* **2003**, 52 (8), 1262-1274.
- (18) Sastry, M. Correlation of C 1s binding energies in organic molecules with atomic charge calculated using a modified Sanderson formalism. *J. Electron. Spectrosc. Relat. Phenom.* **1997**, 85 (1–2), 167-174.
- (19) Chen, G.; Yang, X.; Wang, R.; Fane, A. G. Performance enhancement and scaling control with gas bubbling in direct contact membrane distillation. *Desalination* **2013**, 308 (0), 47-55.
- (20) Feng, L.; Zhang, Y.; Xi, J.; Zhu, Y.; Wang, N.; Xia, F.; Jiang, L. Petal Effect: A Superhydrophobic State with High Adhesive Force. *Langmuir* **2008**, 24 (8), 4114-4119.
- (21) Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Öner, D.; Youngblood, J.; McCarthy, T. J. Ultrahydrophobic and Ultralyophobic Surfaces: Some Comments and Examples. *Langmuir* **1999**, 15 (10), 3395-3399.
- (22) El-Bourawi, M. S.; Ding, Z.; Ma, R.; Khayet, M. A framework for better understanding membrane distillation separation process. *J. Membr. Sci.* **2006**, 285 (1–2), 4-29.
- (23) Wang, X.; Ding, B.; Sun, G.; Wang, M.; Yu, J. Electro-spinning/netting: A strategy for the fabrication of three-dimensional polymer nano-fiber/nets. *Prog. Mater. Sci.* **2013**, 58 (8), 1173-1243.

Figure 1. Schematic of an ideal MD membrane with a lotus leaf-like superhydrophobic selective layer and a scaffold-like nanofiber support layer.

Figure 2. The XPS C 1s core-level spectra of (A) PVDF nanofiber membrane, (B) modified silica and (C) modified SiO₂-PVDF composite membrane.

Figure 3. Photo images, FSEM surface morphologies of PVDF nanofiber membrane (A) and superhydrophobic silica-PVDF composite membrane (B) and corresponding schematic illustrations of nanofiber and superhydrophobic composite membrane (C and D)

Figure 4. Variation of contact angle and sliding angles of composite membranes with different nano-particle sizes and various electrospinning times: (A) membrane fabricated by PVDF/ small FS10-SiO₂ mixture; (B) membrane fabricated by PVDF/ large FS10-SiO₂ mixture

Figure 5. Continuous DCMD tests of the original electrospun PVDF membrane (A), S-PVDF (B), L-PVDF composite membranes (C) and commercial PVDF (D) (3.5 wt% NaCl solution as feed, $T_f=333$ K, $T_p=293$ K)

Figure 6. Surface and cross-section morphologies of fabricated electrospun membranes after continuous DCMD tests: (A and B) PVDF nanofiber membrane; (C and D) S-PVDF and (E and F) L-PVDF. Inserted images are the water contact pictures of corresponding used nanofibrous membranes.

Figure 7. Schematic illustration of PVDF nanofiber membrane surface (A) and superhydrophobic PVDF membrane surface (B) used in the DCMD configuration.

Table 1. Characteristic properties of PVDF nanofiber membrane, S-PVDF, L-PVDF composite membranes and commercial PVDF membranes.

Membrane ID	PVDF	S-PVDF	L-PVDF	Commercial PVDF
Contact angle (°)	142.8 ± 1.4	156.3 ± 2.0	153.9 ± 1.9	135.0 ± 1.3
Surface mean pore size (µm)	0.68 ± 0.03	0.69 ± 0.02	0.77 ± 0.02	0.28 ± 0.01
Surface max pore size (µm)	1.27 ± 0.02	1.23 ± 0.01	1.22 ± 0.01	0.46 ± 0.01
Thickness (µm)	115 ± 8	102 ± 15	129 ± 8	111 ± 1
Bulk porosity (%)	85 ± 1	82 ± 2	83 ± 1	62 ± 1
LEPw(bar)	1.13 ± 0.08	1.75 ± 0.05	1.79 ± 0.07	2.25 ± 0.17
Tensile modulus Et (Mpa)	42 ± 5	35 ± 2	33 ± 2	10 ± 2
Tensile at break σB (Mpa)	9.6 ± 0.9	3.7 ± 0.6	4.2 ± 0.6	4.7 ± 1.8
Strain at break δ (%)	160 ± 3	99 ± 7	87 ± 22	19 ± 11