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**Anisotropic performance of a superhydrophobic polyvinyl difluoride
membrane with corrugated pattern in direct contact membrane distillation**

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Abstract

20 A novel surface-corrugated superhydrophobic polyvinylidene fluoride (PVDF) membrane (C-
21 PVDF) was prepared for direct contact membrane distillation (DCMD) using a micromolding
22 phase separation (μ PS) method. The membrane showed a static contact angle of $159.0 \pm 4.0^\circ$.
23 However, dynamic measurements of the sliding angles revealed a lower value of $9.1 \pm 0.8^\circ$
24 when a water droplet slides in parallel to the ridge, and a higher value of $14.6 \pm 1.6^\circ$ if
25 perpendicular to the ridge. This anisotropic property was also reflected in the DCMD fluxes
26 for both feed of deionized water and 4.0 wt.% NaCl solution: in case the feed flows in parallel
27 to the ridge, a higher flux is resulted than it flows perpendicular to the ridge. Anisotropic MD
28 performance cannot be explained by the Dusty-Gas model because the average characteristics
29 of the membrane in the model are intrinsically the same for both flow modes. Instead,
30 anisotropic wetting and sliding in the parallel and perpendicular orientation revealed that the
31 MD performance has both thermodynamic and hydrodynamic origins.

32 **Keywords:** superhydrophobic; micromolding phase separation; patterned surface; membrane
33 distillation; anisotropic

34

35 1. Introduction

36 Membrane distillation (MD) is a thermal-driven desalination process utilizing hydrophobic
37 porous membranes [1, 2]. When low grade heat is available, MD can outperform other
38 membrane desalination technologies in terms of high rejection, low capital and operational cost,
39 particularly in treating highly saline liquids [3, 4]. However, limitation in fouling/scaling of
40 hydrophobic membranes has largely constrained the progress of MD in practice.

41 To solve the fouling/scaling issues in MD membranes, two approaches have normally been
42 exploited: (1) A standard practice via optimization of the process parameters, such as aeration
43 [5], flow rate [6], addition of antiscalants [7], and acidic cleaning of the scaled membrane [8].
44 (2) Surface engineering for MD membrane from hydrophobic to superhydrophobic or
45 omniphobic. This was pursued as the key solution to improve the fouling and scaling resistance.
46 The development of engineered surface followed the trend from random coating [9], to coating
47 of nanofiber with/without nanoparticles [9-12] to precisely controlled patterned surface [13,
48 14]. Besides physical modification, the final polishing of the surface is critical as well, mostly
49 by surface deposition or grafting of fluorine-containing chemicals [9, 11, 15-17] or by CF₄
50 plasma treatment [18-22]. The superhydrophobic or omniphobic properties via combination of
51 physical and chemical modification hold potential to enhance fouling and scaling resistance by
52 mimicking the lotus leave effect [11, 23].

53 Controlled pattern surface has been recently viewed as a novel platform to understand the
54 fouling/scaling resistance of hydrophobic membrane. Surface patterning of hydrophilic
55 membranes in pressurized filtration has been extensively investigated for microfiltration,
56 ultrafiltration, and reverse osmosis/nanofiltration [24-26]. The resultant increase in the surface

57 area [27] and shear stress near the membrane surface [24, 28] contribute to increased water
58 flux and improved fouling resistance. A computational fluid dynamics simulation and
59 experimental verification proved that the surface pattern induces high shear stress which
60 decreases the adherence of foulants to the membrane [28, 29].

61 For hydrophobic membranes, the effect of micropatterns on MD performance has been
62 demonstrated, but far from understood. Membranes with millimeter scale patterns prepared
63 using non-woven spacers showed stable MD flux in processing real seawater and concentrated
64 seawater; extra turbulence created by the corrugated surface structure was attributed to the
65 performance [30]. Nanoimprinted MD membranes with a groove pattern showed a weak
66 hydrophobic interaction with BSA proteins and hence low fouling propensity which was
67 supported by static thermodynamic analysis of adsorption propensity [14]. Recent development
68 of micropillared superhydrophobic membrane showed excellent scaling resistance [4, 13, 31,
69 32].

70 To implementing patterned MD membrane in large-scale use, it is highly desirable to
71 develop a cheap flexible mold with large dimension is highly expected. Therefore, we aim to
72 explore a new robust and economic method to prepare patterned superhydrophobic membrane
73 and explore their potential as MD membrane. The MD performance of membranes with
74 microscale corrugated surface has not been reported previously. In this communication, a
75 polymeric corrugated substrate (Fig. 1) is used to prepare superhydrophobic polyvinyl fluoride
76 (PVDF) microporous membrane for direct contact membrane distillation (DCMD).
77 Unexpected flux differentiation was, for the first time, observed: MD fluxes are different
78 between a flow parallel to the ridge and a flow perpendicular to the ridge. This anisotropic flux

79 behavior was correlated to the difference in sliding angles and was possible due to the
80 hydrodynamic disruption at the water-air-solid interface. The results provide a new insight to
81 the potential of hydrophobic micropatterned membranes in membrane distillation.

82

83 **2. Materials and methods**

84 2.1 Materials and chemicals

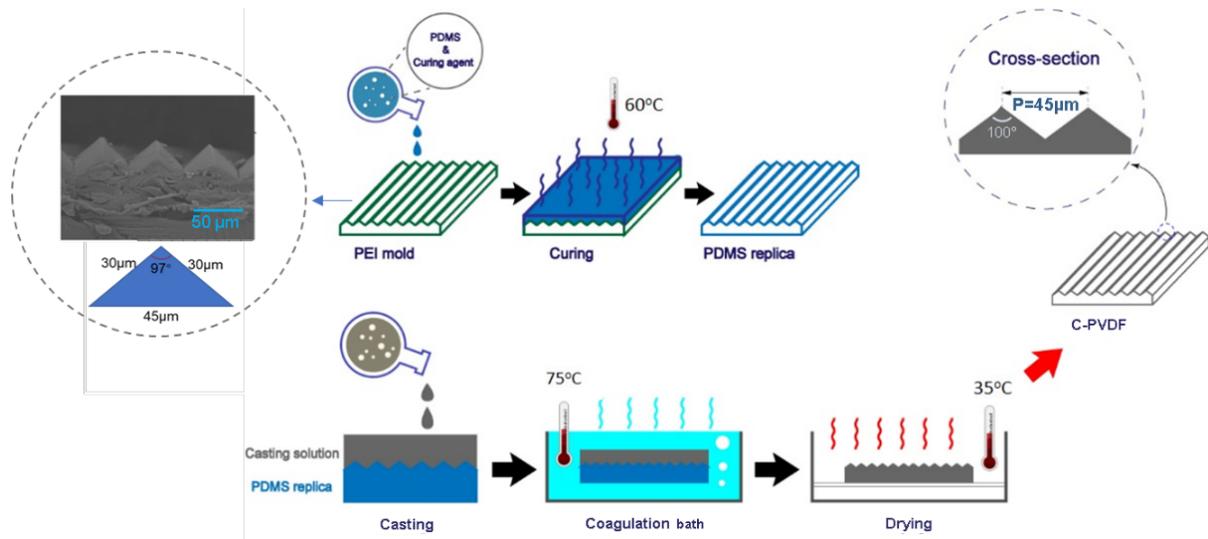
85 The polymer powder, PVDF (Solef 1015) was supplied by Solvay. N, N-
86 Dimethylacetamide (DMAc, AR) and Diethylene glycol (DEG, AR) were provided by
87 Sinopharm Chemical Reagent Co. Ltd. PDMS (Polydimethylsiloxane) and the curing agent
88 (SYLGARD 184) were purchased from Dow Corning Co. Ltd and without further purification
89 before usage. The PEI (polyetherimide) grating template with a corrugated surface was
90 purchased from Suzhou Crystal Silicon Electronic and Technology Co. Ltd. The dimensions
91 of the grating template are showed in Fig. 1.

92 2.2 Preparation of surface patterned PVDF membranes via μ PS

93 **Preparation PDMS mold:** Oligomer PDMS and the curing agent (SYLGARD 184, Dow
94 Corning Co. Ltd) were pre-mixed at a weight ratio of 10:1. After de-gassing in vacuum for 10
95 min, the mixture was cast onto the PEI mold. Then the mold and the PDMS solution was
96 transferred into a vacuum oven and cured for 3 hours at 60 °C. The PDMS replica was then
97 peeled off and stored in a clean container. The entire process was carried out in a clean room.

98 **Preparation of PVDF membrane:** Homogeneous PVDF casting solution PVDF/DEG/DMAc
99 (15/27.4/57.6 wt.%) was prepared in a flask at 90°C with vigorous mechanical stirring for 12
100 h. After filtered using a metal filter of 40 μ m, the solution was deaerated at 90°C. The solution

101 was then cast on the PDMS mold to a film of 250 μm thickness using a tailor-made stainless-
 102 steel casting knife. The PDMS replica was pre-warmed in the oven at 65 $^{\circ}\text{C}$ to avoid any
 103 inhomogeneity in temperature during casting. Subsequently, the cast polymer film was exposed
 104 to water vapor for 10s (10 cm above coagulation water bath, 75 $^{\circ}\text{C}$) and immersed in a
 105 coagulation bath for 15 minutes to induce precipitation and remove of DEG and DMAc residue.
 106 The membrane was further rinsed with water to remove traces of solvent and additives. Before
 107 being dried in the oven at 35 $^{\circ}\text{C}$ for 24h, the membrane was rinsed using ethanol. The resultant
 108 membrane was coded as patterned corrugated PVDF membrane (C-PVDF). Fig. 1 shows the
 109 procedure for the fabrication of patterned PVDF membranes and details are as follows.



110
 111 Fig. 1 Schematic for the fabrication of corrugation patterned PVDF membranes (C-PVDF). The patterned
 112 PVDF membrane has surface corrugation with the dimension of 45 μm (Period).
 113

114 2.3 Membrane characterization

115 The membrane morphology was examined by scanning electron microscopy (SEM)
 116 (HITACH TM-1000 and FEI Nova Nano SEM 450). Prior to imaging, membrane samples were
 117 coated with a thin layer of gold using a sputter coater. Water contact angle (CA) and sliding

118 angle (SA) of the membranes were measured using a contact angle goniometer (Maist Drop
119 Meter A-100P) via the sessile drop method. The tilt angle at which the droplet started rolling
120 off the surface was noted as the sliding angle. Pore size was analyzed using porometry (Porolux
121 1000) [31, 33].

122 2.4 MD performance

123 Direct contact MD (DCMD) experiments were performed on a bench-scale membrane test
124 apparatus [23, 34]. Both deionized water and 4 wt.% NaCl solution were tested as the feed and
125 permeate at 60 °C and 20 °C respectively. The patterned side of the C-PVDF membrane was
126 in contact with the feed. Conductivity of the permeate was measured by a conductivity sensor
127 (HQ14d, Hach, CO). The flux (J , kg/m²·h) was calculated based on Eq. (1):

$$128 \quad J = \Delta m / A \Delta t. \quad (1)$$

129 Where Δm (kg) is the amount of water transported from the feed to the permeate, Δt the interval
130 of the collection (h) and A the membrane area (m²).

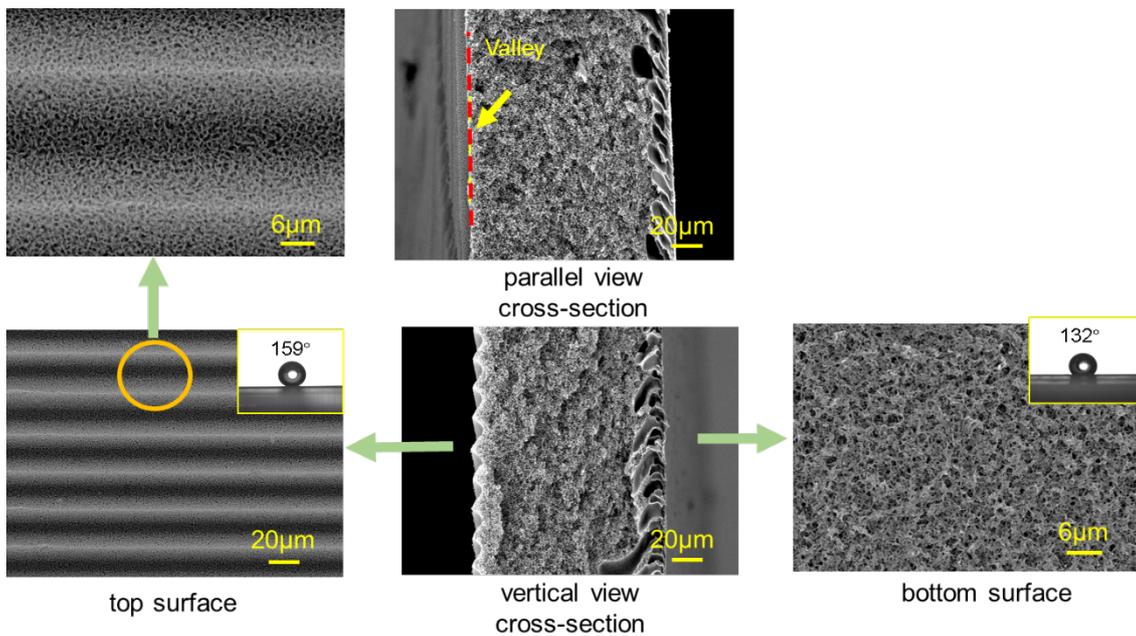
131 3. Results and discussion

132 3.1 Morphology of the C-PVDF membrane

133 Fig. 3 shows the SEM images of the top, bottom and cross-section of the C-PVDF
134 membrane. The membrane shows a porous top and bottom surface, as well as a microporous
135 cross-section. The ridges and valleys of the corrugated C-PVDF membranes is characterized
136 as open porous with no visual variations between the ridge and valley (Fig. 2, inserts,
137 magnified). For clarity, the patterned surface facing the feed, is named as the top membrane
138 surface in this work. Fig. 2 shows that the corrugated surface of the C-PVDF membrane (i.e.
139 the top surface) was the one in contact with the PDMS replica during membrane formation.

140 Upon immersion precipitation, the phase separation started from the top, open surface of
 141 the polymer solution (opposite to the PDMS mold); instantaneous demixing occurred at the
 142 water/polymer solution interface, resulting in a finger-like macrovoid structure (i.e. C-PVDF
 143 cross-section in Fig. 2). However, below this surface, the solvent and additives in the polymer
 144 solution close to the PDMS replica had to diffuse across the whole membrane into the water
 145 bath, thus allowing enough time for the polymer-lean phases to grow and eventually enlarge
 146 into microporous structure [35-38]. The interconnected porous structure in the smooth and
 147 corrugated surfaces was resulted from the competition between the solid-liquid phase
 148 separation and liquid-liquid separation for a semi-crystalline polymer [39].

149



150

151 Fig. 2 SEM images of C-PVDF membranes. Notice the parallel view and the vertical view of the cross-
 152 section. The top surface in this experiment was the surface facing the feed, but in preparation process, it
 153 was in contact with the PDMS mold.

154

155 As listed in Table 1, the C-PVDF membrane had a thickness of $\sim 160 \mu\text{m}$, and a mean pore
156 size of $0.101 \mu\text{m}$. The membrane is relatively thick comparing to the commercial PVDF
157 membranes (of $125 \mu\text{m}$) [33]. However, this is adjustable if needed. The membrane is
158 superhydrophobic with a static contact angle of $159 \pm 4^\circ$. Interestingly, when measuring the
159 sliding angle, a striking difference was found: when the water droplets rolled in parallel with
160 the ridge, a sliding angle of $9.1 \pm 0.8^\circ$ was observed, but a sliding angle of $14.6 \pm 1.6^\circ$ was
161 observed when the water droplets rolled perpendicular to the ridge. To distinguish these two
162 flow modes, we thus define the first as C-PVDF-p and the second mode as C-PVDF-v (using -
163 v instead of -p for clarity). Intuitively, C-PVDF-v mode has slightly higher resistance to the
164 sliding of water droplets than in C-PVDF-p mode. Since the difference in sliding angles are
165 small, no difference would be expected for both orientations. In the following sessions, we will
166 discuss the difference induced by this minor difference on the MD performance.

167

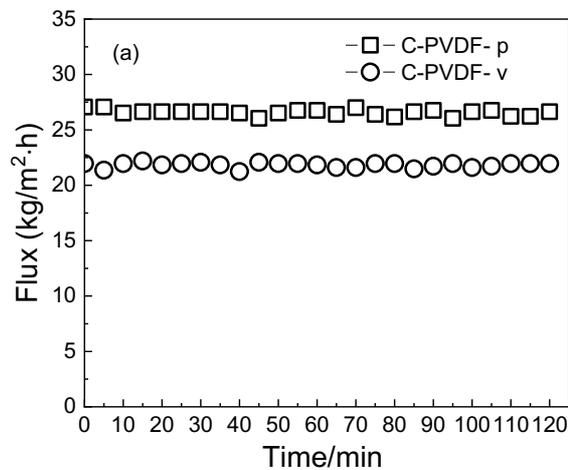
168 Table 1. Characteristics of the C-PVDF membrane.

Characteristics	Value
CA of top surface ($^\circ$)	159 ± 4
CA of bottom surface ($^\circ$)	132 ± 3
Mean pore size (μm)	0.101 ± 0.010
Thickness (μm)	160 ± 5
Sliding angle-p ($^\circ$)	9.1 ± 0.8
Sliding angle-v ($^\circ$)	14.6 ± 1.6

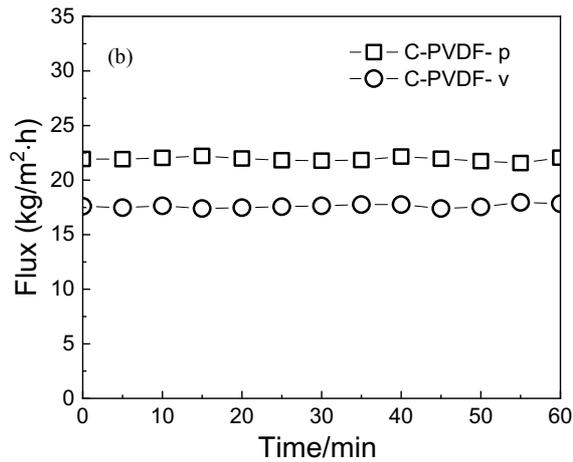
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170 3.2 MD performance

171 The DCMD fluxes with both parallel (C-PVDF-p) and perpendicular (C-PVDF-v) modes
172 are shown in Fig. 3a using deionized water as feed. In 120 min, an obviously higher constant
173 flux of 26.6 kg/m²·h was observed in the C-PVDF-p mode than in the C-PVDF-v mode (21.6
174 kg/m²·h). This means that when water flows in parallel to the ridge, there is an increase of
175 about 25% in flux compared to the case when water flows perpendicular to the ridge. To
176 confirm this observation, a simulated seawater containing 40 g/L NaCl as the feed (Fig. 3b)
177 was tested; again, the flux of the C-PVDF-p mode was found about 10% higher than that of the
178 C-PVDF-v mode. No obvious flux decrease was observed for both C-PVDF-p and C-PVDF-v
179 membranes in a test for 60 minutes due to nearly constant salt concentration in the feed.



180



181

182 Fig. 3 Effect of the flow directions in relation to the corrugation pattern on DCMD Fluxes of C-PVDF

183 membranes. C-PVDF-p represents feed flow in parallel to the ridge; C-PVDF-p represents feed flow in

184 perpendicular to the ridge. (a) feed: deionized water; (b) 40 g/L NaCl solution. Feed temperature: 60.0±1.0

185 °C; permeate temperature: 20.0±1.0 °C. Flow rate of both feed and permeate: 600 ml/min. Rejection of the

186 membrane for NaCl was 100% using 40 g/L NaCl solution as the feed.

187

188 3.3 Analysis for the origin of anisotropy flux

189 In average, the flow direction to the orientation of the ridge in principal does not affect the

190 mass transfer in MD, thus the flux. According to the Gas-Dusty model [40] , the MD flux is

191 linearly correlated to the water vapor pressure difference across the membrane and the

192 membrane material and morphology, but not directly related to the flow direction. Because of

193 the membrane was exactly the same, thermal conductivity is also not directly related to the

194 flow direction. Theoretically, the flux should be independent from the flow, either in parallel

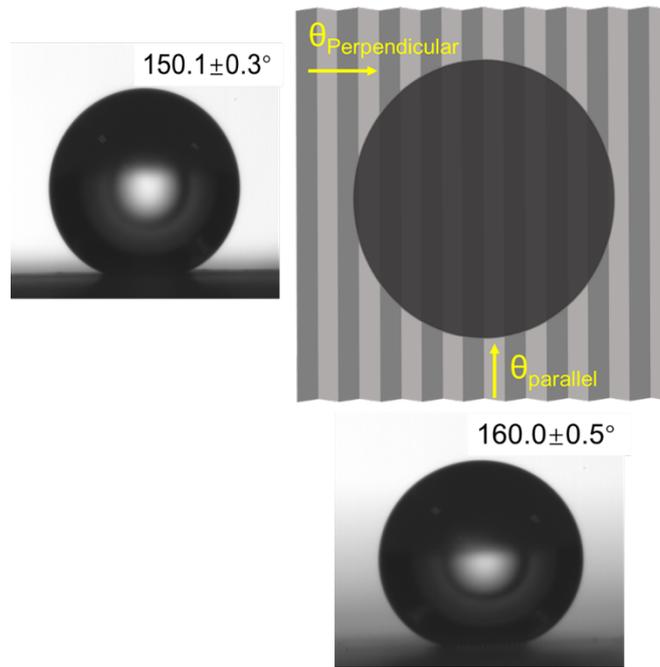
195 or perpendicular to the ridge. However, the experimental results do not obey the conventional

196 Gas-Dusty model.

197 Previous studies showed that a superhydrophobic membrane had an increased MD flux in

198 comparison to the pristine one with similar morphology [20, 41] [42]. The observed high MD
199 flux was understood by taking into account of enlarged evaporation surface area in the
200 superhydrophobic PVDF membranes [20, 41]. However, for the corrugated surface studied in
201 this work, the same static contact angles were observed regardless of the flow direction (Table
202 1). Thus, previous theory on the enlarged evaporation area was not applicable from the point
203 view of the static contact angle as two directions would show the same evaporation area.
204 However, evaporation area was still one of the important key factors in determining MD flux
205 [17].

206 Anisotropic wetting of patterned surfaces has been discovered in previous researchers [43-
207 45], however mainly on a dense surface structure, not on a porous surface structure as reported
208 in this paper. Within similar dimensions, the wetting anisotropy ($\Delta\theta$) is strongly related to the
209 groove height, but not greatly depended on period and width [46]. Fig. 4 shows that the wetting
210 anisotropy ($\Delta\theta$) of our C-PVDF membrane is about 10° . with great angle at the parallel view.
211 This anisotropic phenomenon is similar to literature reported results, but to a significantly
212 lesser extent [43-45]. This may be related to the polymer materials we used in this experiment,
213 PVDF, and the surface porosity in the membrane.



214

215 Fig. 4 Images of water droplets on corrugated PVDF membrane surface showing slight
 216 anisotropic wetting at parallel and perpendicular directions (Top right hand picture only for
 217 schematic demonstration). Note that the view point for measurement is the same as those in
 218 flow. The water contact angle measured from parallel view is slightly larger than greater than
 219 that measured from the perpendicular view.

220

221 Because high energy is required for surpassing the energy barrier created by anisotropic
 222 geometry, the contact angle is raised for movement of the contact lines [43]. This results in a
 223 higher contact angle at the parallel view, but a lower angle at the perpendicular view. The other
 224 anisotropy is demonstrated in the sliding angles as listed in Table 1. Much lower sliding angle
 225 was observed at parallel direction, corresponding to the greater water contact angle at the
 226 parallel view. There seems a strong correlation between the thermodynamic measurement
 227 (contact angle) and dynamics measurement (sliding angle). By evaluating the sliding angle, a
 228 simple calculation shows that the drag force in parallel to the ridge is about 0.62 ($< 2/3$) of that

229 in perpendicular direction (the ratio of the drag force in two directions = $\sin(9.1^\circ)/\sin(14.6^\circ)$
230 = 0.62). Intuitively, a small difference of a few degrees in the sliding angle means a small
231 difference in the drag force, but in reality, water droplets encounter much less drag force in the
232 parallel direction (about 38%) than in the perpendicular direction. This direct us to a hypothesis
233 for the flux differentiation at two directions with a hydrodynamic interfacial origin. A
234 quantitative correlation is possible if direct observation of the interface is realized. Since this
235 experimental observation is out of scope of the conventional static view on the hydrophobic
236 membrane surface, a new hydrodynamic analysis will add a new dimension to a more
237 comprehensive understanding of the interface in membrane distillation.

238 The finding of anisotropic performance for MD membranes with corrugated pattern is
239 unexpected, but intriguing. Scientific understand of such phenomenon is important for future
240 design of patterned surfaces for high performance. Increase in the flux would result in reduced
241 membrane surface area, small footprint as well as capital investment. The fouling/scaling
242 behavior of surface patterned membrane might also be improved at optimized ridge
243 height/period/angle for corrugated surface.

244 **4. Conclusions**

245 Superhydrophobic polyvinylidene fluoride (PVDF) membranes with well-controlled
246 corrugated pattern were prepared via a micromolding phase separation technology. The
247 membrane showed a high static contact angle of 159 ± 4 and an average pore size of $0.1 \mu\text{m}$.
248 Surprising anisotropic MD flux was observed when the feed flows in a parallel and
249 perpendicular orientation to the ridge of the pattern. For both deionized water and NaCl

250 solution, obviously higher flux was found in parallel orientation. This deviation cannot be
251 explained by the Dusty-Gas model because the average characteristics of the membrane in the
252 model are intrinsically the same for both flow modes. Instead, anisotropic wetting and sliding
253 in the parallel and perpendicular orientation revealed both thermodynamic and hydrodynamic
254 origins of our new findings. The present observation has revealed the limitation of the
255 conventional MD model in analysis of micro-patterned superhydrophobic surface.

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