

1 **3D Structure Enhancers Based on Functionalized MIL-53(Al) for Improved**
2 **Dimethyl Carbonate/Methanol Pervaporative Separation**

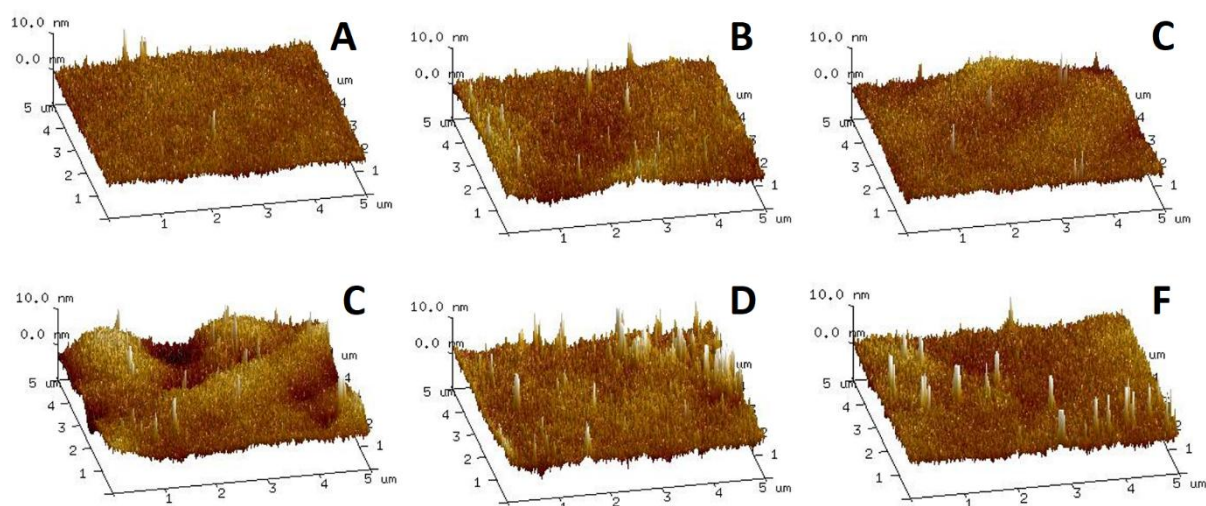
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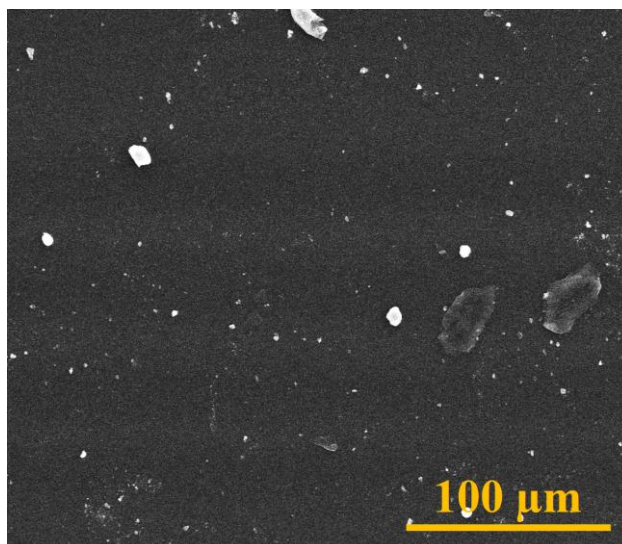
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19 Figure S1. AFM micrographs of surfaces of pristine PDMS (A). PDMS/MIL-53(Al) 5 wt% (B).
20 PDMS/MIL-53(Al) 10 wt% (C). PDMS/MIL-53(Al) 15 wt% (D). PDMS/NH₂-MIL-53(Al) 5 wt% (E).
21 and PDMS/NHOCOFCF₃-MIL-53(Al) 5 wt% (F) membranes.
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24 Figure S2. SEM micrographs of the surface of PMDS/MIL-53(Al) 15 wt%.

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26 Table S1. Value of surface roughness (R_A) of pristine and heterogeneous PDMS based membranes.

| Membranes | R_A [nm] |
|---|------------------------------|
| PDMS pristine | 0.6±0.1 |
| PDMS/MIL-53(Al) 5 wt% | 0.8±0.1 |
| PDMS/MIL-53(Al) 10 wt% | 0.7±0.1 |
| PDMS/MIL-53(Al) 15 wt% | 1.3±0.1 |
| PDMS/NH ₂ -MIL-53(Al) 5 wt% | 1.1±0.1 |
| PDMS/NHOCOCF ₃ -MIL-53(Al) 5 wt% | 0.8±0.1 |

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30 Table S2. Comparison of experimental data for separation of DMC/MeOH mixture (50 wt%:50 wt%)
 31 with increased the content of water in the feed mixture for pristine PDMS membrane.

| Water content in feed [wt%] | MeOH content [wt%] | | DMC content [wt%] | |
|---------------------------------------|---------------------------|-----------------|--------------------------|-----------------|
| | feed | permeate | feed | permeate |
| 0.1 | 49.5 | 30.5 | 50.4 | 69.1 |
| 0.7 | 49.9 | 29.9 | 49.5 | 69.6 |
| 1.0 | 50.6 | 30.0 | 48.3 | 69.4 |
| 1.5 | 51.1 | 29.8 | 47.4 | 69.5 |
| 2.2 | 51.7 | 29.5 | 46.2 | 69.6 |
| 3.3 | 52.6 | 29.1 | 44.2 | 69.8 |
| 4.2 | 51.6 | 28.8 | 44.2 | 69.9 |
| 5.9 | 50.7 | 28.6 | 43.4 | 69.6 |

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33 Table S3. Hansen's Solubility Parameters for mixtures of DMC/MeOH containing increasing amounts
 34 of water. Pervaporation performed with pristine PDMS membrane

| Mixture [wt%] | δ_d [MPa ^{0.5}] | δ_p [MPa ^{0.5}] | δ_h [MPa ^{0.5}] |
|---|----------------------------------|----------------------------------|----------------------------------|
| H ₂ O: 0.1 DMC: 50.4 MeOH: 49.5 | 15.3 | 10.4 | 16.5 |
| H ₂ O: 0.7 DMC: 49.5 MeOH: 49.9 | 15.3 | 10.5 | 16.7 |
| H ₂ O: 1.0 DMC: 48.3 MeOH: 50.6 | 15.3 | 10.5 | 16.9 |
| H ₂ O: 1.5 DMC: 47.3 MeOH: 51.1 | 15.3 | 10.6 | 17.1 |
| H ₂ O: 2.2 DMC: 46.2 MeOH: 51.7 | 15.3 | 10.7 | 17.5 |
| H ₂ O: 3.3 DMC: 44.2 MeOH: 52.6 | 15.3 | 10.8 | 17.9 |
| H ₂ O: 4.2 DMC: 44.2 MeOH: 51.6 | 15.3 | 10.8 | 18.1 |
| H ₂ O: 5.9 DMC: 43.4 MeOH: 50.7 | 15.3 | 10.9 | 18.5 |

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 36 Table S4. Hansen's Solubility Parameters for mixtures of DMC/MeOH containing increasing amounts
 37 of water. Pervaporation performed with pristine PDMS/NHOCOCF₃-MIL-53(Al) membrane.

| Mixture [wt%] | δ_d [MPa ^{0.5}] | δ_p [MPa ^{0.5}] | δ_h [MPa ^{0.5}] |
|---|----------------------------------|----------------------------------|----------------------------------|
| H ₂ O: 0.1 DMC: 49.4 MeOH: 50.5 | 15.3 | 10.5 | 16.6 |
| H ₂ O: 0.7 DMC: 49.5 MeOH: 50.7 | 15.3 | 10.5 | 16.6 |
| H ₂ O: 0.9 DMC: 50.7 MeOH: 48.4 | 15.3 | 10.5 | 16.6 |
| H ₂ O: 1.6 DMC: 51.9 MeOH: 46.5 | 15.3 | 10.4 | 16.5 |
| H ₂ O: 2.4 DMC: 49.9 MeOH: 47.7 | 15.3 | 10.5 | 17.0 |
| H ₂ O: 3.4 DMC: 48.5 MeOH: 48.1 | 15.3 | 10.6 | 17.4 |
| H ₂ O: 4.3 DMC: 46.5 MeOH: 49.2 | 15.3 | 10.7 | 17.8 |
| H ₂ O: 5.8 DMC: 44.4 MeOH: 49.8 | 15.3 | 10.9 | 18.4 |

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40 Table S5. Calculated distance parameters (Δ) between pristine PDMS
 41 and PDMS/NHOCOCF₃-MIL-53(Al) membrane based membranes and the mixture of DMC/MeOH
 42 containing increasing amounts of water.

| pristine PDMS | | PDMS/NHOCOCF₃-MIL-53(Al) | |
|---|--|---|--|
| Mixture [wt%] | Δ [MPa^{0.5}] | Mixture [wt%] | Δ [MPa^{0.5}] |
| H ₂ O: 0.1 DMC: 50.4 MeOH: 49.5 | 16.2 | H ₂ O: 0.1 DMC: 49.4 MeOH: 50.5 | 14.9 |
| H ₂ O: 0.7 DMC: 49.5 MeOH: 49.9 | 16.4 | H ₂ O: 0.7 DMC: 49.5 MeOH: 50.7 | 14.9 |
| H ₂ O: 1.0 DMC: 48.3 MeOH: 50.6 | 16.6 | H ₂ O: 0.9 DMC: 50.7 MeOH: 48.4 | 14.9 |
| H ₂ O: 1.5 DMC: 47.3 MeOH: 51.1 | 16.8 | H ₂ O: 1.6 DMC: 51.9 MeOH: 46.5 | 14.8 |
| H ₂ O: 2.2 DMC: 46.2 MeOH: 51.7 | 17.1 | H ₂ O: 2.4 DMC: 49.9 MeOH: 47.7 | 15.2 |
| H ₂ O: 3.3 DMC: 44.2 MeOH: 52.6 | 17.6 | H ₂ O: 3.4 DMC: 48.5 MeOH: 48.1 | 15.6 |
| H ₂ O: 4.2 DMC: 44.2 MeOH: 51.6 | 17.7 | H ₂ O: 4.3 DMC: 46.5 MeOH: 49.2 | 16.0 |
| H ₂ O: 5.9 DMC: 43.4 MeOH: 50.7 | 18.1 | H ₂ O: 5.8 DMC: 44.4 MeOH: 49.8 | 16.5 |

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