

Efficient pervaporation for ethanol dehydration: Ultrasonic spraying preparation of polyvinyl alcohol (PVA)/ $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet mixed matrix membranes

Huijuan Tong, Qiao Liu*, Nong Xu*, Qing Wang, Long Fan, Qiang Dong, Aiqin Ding

School of Energy, Materials and Chemical Engineering, Hefei University, Hefei
230601, P. R. China

* Corresponding authors, *E-mail addresses*: liuqiao@hfu.edu.cn (Q. Liu), xunong@hfu.edu.cn (N. Xu)



Figure S1. Photograph of the homemade PV device

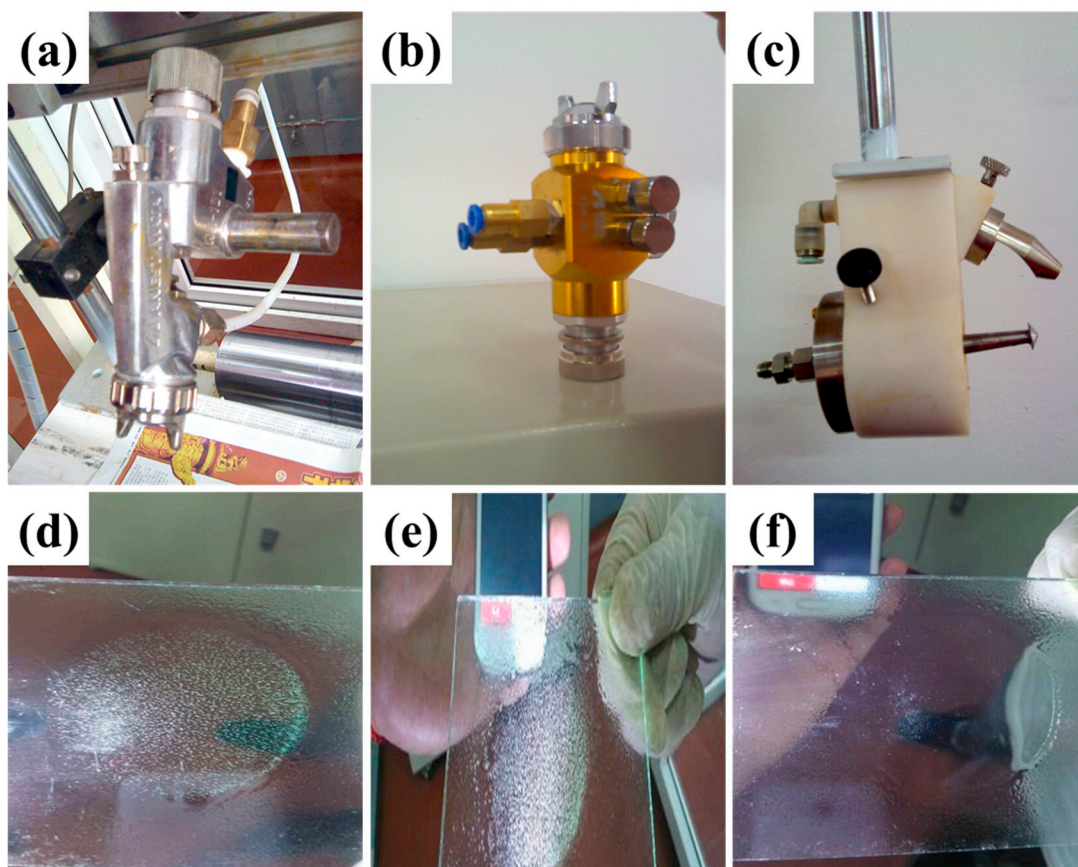


Figure S2. Two different types of gas dynamic spray nozzles, (a) WA-101 and (b) TOF-30-1.5 (Anest-Iwata. Co. Japan), were tried in our spraying processes. (c) ultrasonic spraying nozzle (FSW-6001-L, Funsonic Co. Ltd. China) used in the preparation of the membranes. (d), (e) and (f) were the sprayed fine droplets of the PVA-based solutions on the glass plates after the solutions were puffed out from the WA-101, TOF-30-1.5 and FSW-6001-L, respectively.

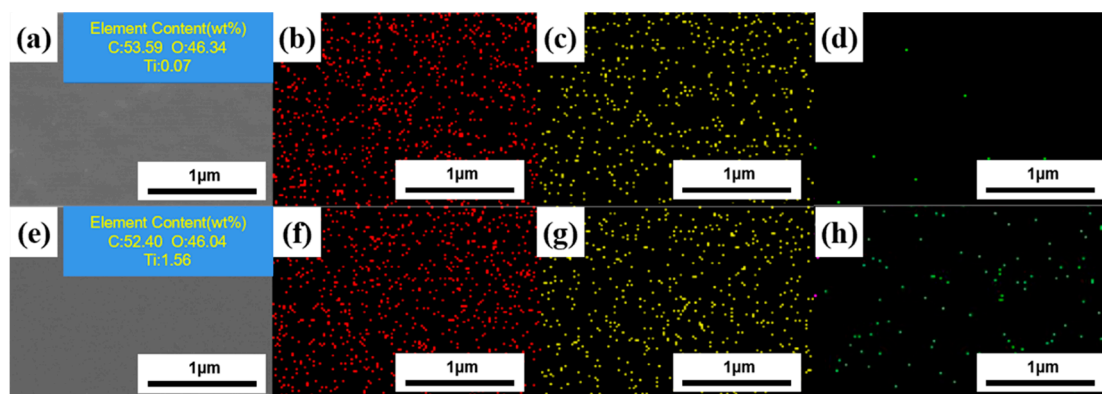














Figure S3. (a) and (e) SEM images, EDX mapping images of (b) and (f) C element, (c) and (g) O element, (d) and (h) Ti element in the PVA and PGM-0 membranes' top-surface, respectively.

Table S1. The PV data for all the prepared composite membranes in this work

| Samples | Water flux ($\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) | Separation factor |
|---------|--|-------------------|
| PVA | 0.26±0.03 | 125.4±36.9 |
| PG | 0.18±0.04 | 133.6±28.4 |
| PGM-0 | 1.21±0.02 | 1126.8±33.7 |
| PGM-1 | 1.05±0.03 | 1108.4±31.2 |
| PGM-2 | 0.95±0.02 | 874.3±29.6 |
| PGM-3 | 0.92±0.03 | 732.8±30.7 |
| PGM-4 | 0.88±0.04 | 687.5±28.4 |
| PGM-5 | 1.08±0.03 | 1084.9±35.4 |
| PGM-6 | 0.96±0.04 | 823.4±29.8 |
| PGM-7 | 1.10±0.02 | 1045.8±32.4 |
| PGM-8 | 1.07±0.03 | 1102.4±36.7 |
| PGM-9 | 0.94±0.04 | 976.4±36.8 |
| PGM-10 | 0.82±0.03 | 875.3±37.5 |

Table S2. Comparison of the PV performance in this work with others

| Membrane | Symbol | Temp. °C | Feed (ethanol wt %) | Water flux ($\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) | Separation factor | Ref. |
|----------------------|---|----------|---------------------|--|-------------------|-----------|
| PVA |  | 40 | 90 | 0.280 | 104 | [1] |
| PVA/ZIF-90 |  | 30 | 90 | 0.268 | 1379 | [2] |
| PVA/SiO ₂ |  | 40 | 85 | 0.145 | 1026 | [3] |
| PVA/GO |  | 45 | 95 | 0.074 | 4281 | [4] |
| CS/siloxane |  | 20 | 90 | 0.47 | 2182 | [5] |
| CS |  | 40 | 96 | 0.004 | 2208 | [6] |
| SA/4A |  | 30 | 90 | 0.111 | 1866 | [7] |
| SA/PVP/PWA |  | 27 | 90 | 0.100 | 1250 | [8] |
| HA/SA/PAN |  | 80 | 90 | 0.90 | 1130 | [9] |
| PAA/PEI/PAN |  | 50 | 85 | 1.00 | 100 | [10] |
| PAA/PEI/PES |  | 40 | 85 | 0.47 | 350 | [11] |
| PGM-0 |  | 30 | 95 | 1.21 | 1127 | This work |

References

- [1] Yeom, C. K.; Lee, K, H. Characterization of sodium alginate and poly(vinyl alcohol) blend membranes in pervaporation separation. *J. Appl. Polym. Sci*, **2001**, *67*(5), 949–959.
- [2] Wei, Z.; Liu, Q.; Wu, C.; Wang, H.; Wang, H. Viscosity-driven in situ self-assembly strategy to fabricate cross-linked ZIF-90/PVA hybrid membranes for ethanol dehydration via pervaporation. *Sep. Purif. Technol.* **2018**, *201*, 256–267.
- [3] Xia, L.; Li, C.; Wang, Y. In-situ crosslinked PVA/organosilica hybrid membranes for pervaporation separations. *J. Membr. Sci*, **2016**, *498*, 263–275.
- [4] Cheng, X.; Cai, W.; Chen, X.; Shi, Z.; Li, J. Preparation of graphene oxide/poly(vinyl alcohol) composite membrane and pervaporation performance for ethanol dehydration. *RSC Adv*, **2019**, *9*(27), 15457–15465.
- [5] Lin, Y.; Ho, J. C.; Lin, K. Y. A.; Tung, K. L.; Chung, T. W.; Lee, C. C. A drying-free and one-step process for the preparation of siloxane/CS mixed-matrix membranes with outstanding ethanol dehydration performances. *Sep. Purif. Technol*, **2019**, *221*, 325–330.
- [6] Uragami, T.; Matsugi, H.; Miyata, A. T. Pervaporation characteristics of organic-inorganic hybrid membranes composed of poly(vinyl alcohol-co-acrylic acid) and tetraethoxysilane for water/ethanol separation. *Macromolecules*, **2005**, *38*(20), 8440–8446.
- [7] Zhao, J.; Fang, C.; Zhu, Y.; He, G.; Pan, F.; Jiang, Z.; Zhang, P.; Cao, X.; Wang, B. Manipulating the interfacial interactions of composite membranes via a

mussel-inspired approach for enhanced separation selectivity. *J. Mater. Chem. A*, **2015**, 3(39), 19980–19988.

[8] Magalad, V. T.; Gokavi, G. S.; Ranganathaiah, C.; Burshe, M. H.; Han, C.; Dionysiou, D. D.; Nadagouda, M. N.; Aminabhavi, T. M. Polymeric blend nanocomposite membranes for ethanol dehydration-effect of morphology and membrane-solvent interactions. *J. Membr. Sci.*, **2013**, 430, 321–329.

[9] Gao, C.; Zhang, M.; Ding, J.; Pan, F.; Jiang, Z.; Li, Y.; Zhao, J. Pervaporation dehydration of ethanol by hyaluronic acid/sodium alginate two-active-layer composite membranes. *Carbohydr. Polym.*, **2014**, 99, 158–165.

[10] Zhang, G.; Song, X.; Ji, S.; Wang, N.; Liu, Z. Self-assembly of inner skin hollow fiber polyelectrolyte multilayer membranes by a dynamic negative pressure layer-by-layer technique. *J. Membr. Sci.*, **2008**, 325(1), 109–116.

[11] Zhang, G.; Gu, W.; Ji, S.; Liu, Z.; Peng, Y.; Wang, Z. Preparation of polyelectrolyte multilayer membranes by dynamic layer-by-layer process for pervaporation separation of alcohol/water mixtures. *J. Membr. Sci.*, **2006**, 280(1-2), 727–733.