Electronic Supplementary Information (ESI)

Non-activation ZnO array as buffering layer to fabricate strongly adhesive metal-organic framework/PVDF hollow fiber membranes

Contents

- 1. Experimental detail
 - 1.1 Materials
 - 1.2 Ammoniation of PVDF membrane
 - 1.3 Synthesis of NA-ZnO/PVDF
 - 1.4 Synthesis of ZIF-8/PVDF
 - 1.5 Synthesis of ZIF-7/PVDF
 - 1.6 Characterization
 - 1.7 Gas permeances of MOF membrane
- 2. Results and Discussions
- 2.1 Characterization
- 2.2 Gas separation performance comparison
- 3. Reference

1. Experimental Detail

1.1 Materials

Zinc nitrate hexahydrate and zinc chloride were purchased from Changzheng Chemical Reagent Co., Ltd, China. 2-methylimidazole and benzimidazole were supplied by Hangzhou Banghua Chemical Co., Ltd, China. The solvents of methanol and N,N-dimethylformamide (DMF) were used without purification. And water used in this study was obtained from a self-made RO-EDI system, in which ion concentration was analyzed by IRIS Intrepid ICP and Metrohm 861 Compact IC and controlled to meet the experimental requirement of $\sigma \leq 0.5 \,\mu\text{S cm}^{-1}$. The PVDF hollow fiber membranes were self-made by typical wet-spinning process.

1.2 Ammoniation of PVDF membrane

The PVDF membrane was immersed into the autoclave filled by ethanediamine solution (25 %, v/v), then the autoclave was heated at 423 K for 20 h. After cooling, the ammoniated PVDF membrane was washed by water for several times, and then dried at room temperature.

1.3 Synthesis of NA-ZnO/PVDF

For formation of the NA-ZnO array layer on the PVDF hollow fiber. 0.245 g 2methyl-imidazole, 0.135 g sodium formate and 0.592 g zinc nitrate hexahydrate were dissolved in 15 ml methanol by ultrasound. The PVDF hollow fiber was immersed vertically in the solution and contained by an autoclave. Then, the autoclave was subjected to heat-treatment at 353 K or 423 K for 12 h. After reaction was complete, NA-ZnO/PVDF was taken out and washed by methanol for several times and dried at atmosphere.

1.4 Synthesis of ZIF-8/PVDF

2-methyl-imidazole (0.491 g), sodium formate (0.271 g) and zinc chloride (0.542 g) were dissolved in methanol (30 ml). The NA-ZnO/PVDF was immersed in the solution and then transferred into an autoclave. The membrane was vertically placed to prevent the precipitation of crystals on the surface. The solvothermal condition was

at 383 K for 24 h. After that, the ZIF-8/PVDF was washed by methanol for several times, then dried at atmosphere and activated under vacuum.

1.5 Synthesis of ZIF-7/PVDF

To synthesis of ZIF-7/PVDF, the autoclave was filled with 15 ml DMF solutions, which contained 0.161 g benzimidazole and 0.283 g zinc nitrate hexahydrate. The NA-ZnO/PVDF was uprightly immersed in the solution and heated at 403 K for 48 h. Because of the PVDF hollow fiber was ammoniated, the PVDF was not disslved by DMF. After crystallization, the fabricated ZIF-7/PVDF was washed with DMF for several times and then washed by methanol for another several times. The obtained membrane was dried at atmosphere and activated under vacuum.

1.6 Characterization

Scanning electron microscopy (SEM, TM-1000, Hitachi, Japan) was used to observe the morphology of the membranes. The X-ray diffraction (XRD) patterns were collected on an X'Pert PRO (PNAlytical, Netherlands) diffractometer in the reflection mode with CuK α radiation (40kV, 40mA, λ =0.154056 nm). The FTIR spectroscopy (Nicolet 6700, Thermo Scientific, USA) was used to analyze the chemical structure.

1.7 Gas permeances of MOF membrane

The MOF hollow fiber membranes were sealed in a permeation module by epoxy glue. The SEM was used to measure the diameter of the membrane and the thickness of the MOF layers. Shell side of the membrane was used as the feed side. The data was collected until the system was stable. The permeation side was contacted with the atmosphere (~1 bar), and the pressure at the feed side was 1 bar and controlled by the manometer. The ISF was defined as the ratio of the permeance for the two kinds of gases. The result was calculated from the average of three samples.

2. Results and discussions

2.1 Characterization:



Figure S1.SEM images of (a) ZnO crystals and (b) PVDF hollow fiber after growth.



Figure S2. FTIR of the NA-ZnO synthesized at 353 K.



Figure S3. Cross-section and surface SEM images of (a) (b) NA-ZnO/PVDF synthesized at 353 K and (c) (d) NA-ZnO/PVDF synthesized at 423 K.



Figure S4. XRD patterns of (a) (b) NA-ZnO/PVDF synthesized at 353 K and 423 K, respectively.



Figure S5. (a) (b) surface SEM images of NA-ZnO/PVDF synthesized at 353 K and 423 K after treated by ultrasound (c) low-magnification SEM images of ZIF-8/PVDF (d) SEM images of ZIF-8/PVDF after treated by ultrasound.



Figure S6. XRD patterns of (a) ZIF-7/PVDF and (b) ZIF-8/PVDF.



Figure S7. Cross-section and surface SEM images of CuBTC/PVDF.

2.2 Gas separation performance comparison

Reference	Membrane	T (°C)	Permeance 10 ⁻⁸			ISF	
			$mol/(m^2 \cdot s \cdot Pa)$				
			H_2	N_2	CO_2	H_2/N_2	H_2/CO_2
S1	ZIF-7	200	7.40	1.10	1.10	6.7	6.7
S2	ZIF-7	220	4.55	0.22	0.35	20.7	13.0
S3	ZIF-8	25	6.04	0.52	1.33	11.6	4.5
S4	ZIF-8	25	17.3	1.49	4.45	11.6	3.9
S5	ZIF-8	25	36.0	8.96	14.0	4.0	2.6
S6	ZIF-8	25	5730	370	336	15.5	17.1
S7	ZIF-8	25	43.2	3.53	12.2	12.3	3.5
S8	ZIF-8	30	15.9	1.1	3.1	11.1	5.2
S9	ZIF-8	25	97.4	12.3		7.9	
S10	ZIF-8/Nylon	25	197.0	46.0		4.3	
S11	ZIF-8/PES	60	40.0	4.04		9.9	
This work	ZIF-8	25	201.4	1.11	1.24	18.1	16.3
	ZIF-7	25	235.4	1.16	1.28	20.3	18.4

Table S1. Comparison of separation performances of the prepared membrane in thisstudy with other ZIF-7 and ZIF-8 membranes from literatures.

3. References

(S1) Y. S. Li, F. Y. Liang, H. Bux, A. Feldhoff, W. S. Yang and J. Caro, *Angew. Chem. Int. Ed.* 2010, **49**, 548.

(S2) Y. S. Li, F. Y. Liang, H. Bux, W. S. Yang and J. Caro, *J. Membr. Sci.* 2010, 354, 48.

(3S) H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke and J. Caro, *J. Am. Chem. Soc.* 2009, **131**, 16000.

(S4) M. C. McCarthy, V. V. Guerrero, G. V. Barnett and H. K. Jeong, *Langmuir*, 2010, **26**, 14636.

(S5) Y. Pan and Z. Lai, Chem. Commun 2011, 47, 10275.

(S6) Z. Xie, J. Yang, J. Wang, J. Bai, H. Yin, B. Yuan, J. Lu, Y. Zhang, L. Zhou and C. Duan, *Chem. Commun.*, 2012, **48**, 5977.

(S7) K. Huang, Z. Dong, Q. Li and W. Jin, Chem. Commun. 2013, 49, 10326.

(S8) X. Zhang, Y. Liu, S. Li, L. Kong, H. Liu, Y. Li, W. Han, K. L. Yeung, W. Zhu,W. Yang and J. Qiu, *Chem. Mater.* 2014, 26, 1975.

(S9) X. Zhang, Y. Liu, L. Kong, H. Liu, J. Qiu, W. Han, L. T. Weng, K. L. Yeung andW. Zhu, *J. Mater. Chem. A* 2013, 1, 10635.

(S10) J. Yao, D. Dong, D. Li, L. He, G. Xu and H. Wang, *Chem. Commun.* 2011, 47, 2559.

(S11) L. Ge, W. Zhou, A. Du and Z. Zhu, J. Phys. Chem. C 2012, 116, 13264.