Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Stiff metal-organic framework/polyacrylonitrile hollow fiber composite membranes with high gas permeability

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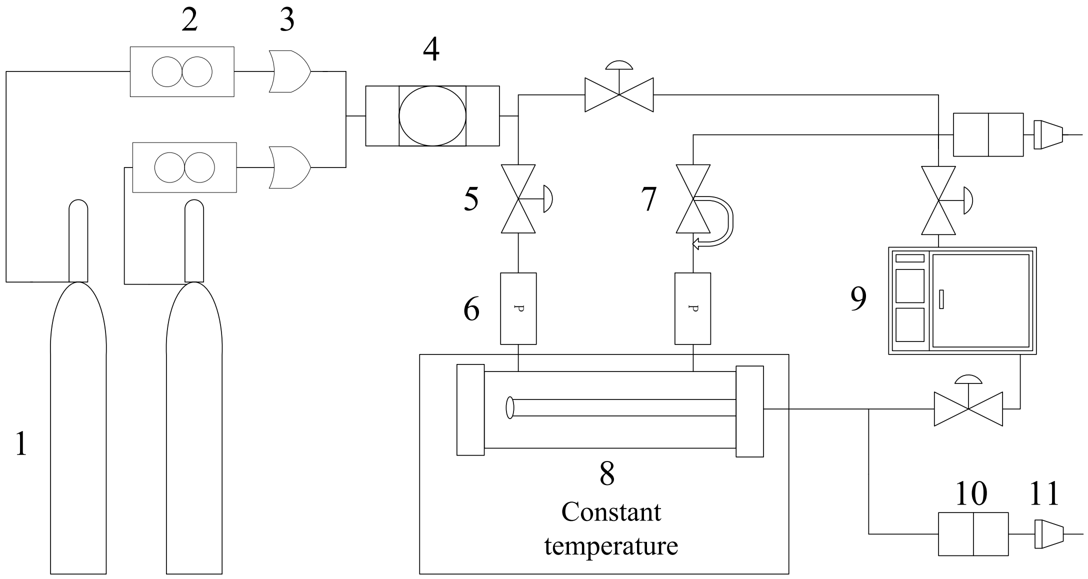

Fig. S1. The experimental setup for both single and mixed gas permeation. (1) Feed gas cylinder, (2) mass flow controller, (3) non-return valve, (4) gas mixer, (5) shut-down valve, (6) pressure gauge, (7) back pressure regulator, (8) permeation cell, (9) gas chromatograph, (10) soap bubble film flow meter, (11) exhaust head.

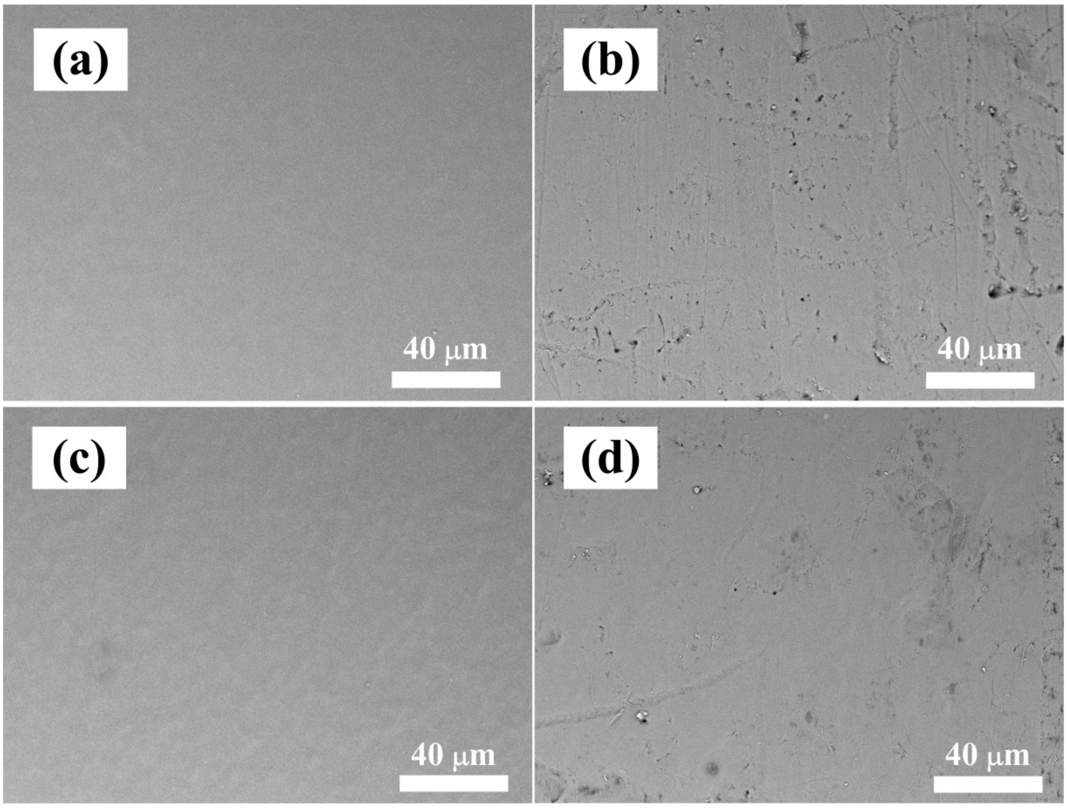

Fig. S2. SEM images of inner and outer surface of the PAN hollow fiber: (a), (b) inner and outer surface of the original PAN hollow fiber; (c), (d) inner and outer surface of the hydrolyzed PAN hollow fiber.

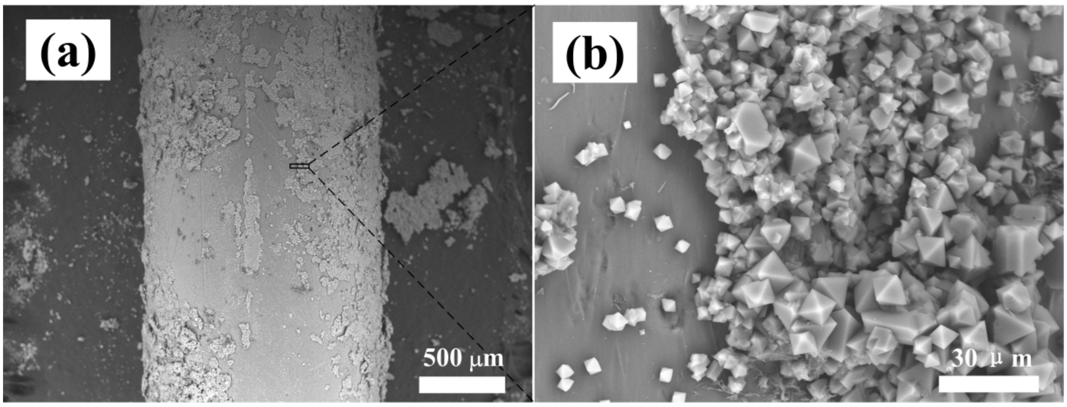

Fig. S3. The low and high magnification SEM images of $Cu_3(BTC)_2$ membrane supported by original PAN hollow fiber.

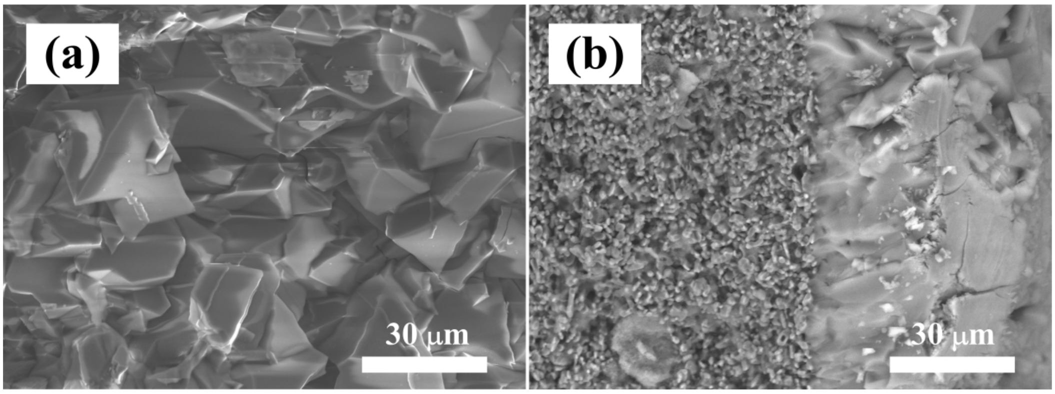

Fig. S4. SEM images of the $Cu_3(BTC)_2$ membrane supported by ceramic substrate: (a) outer surface, (b)cross-section.

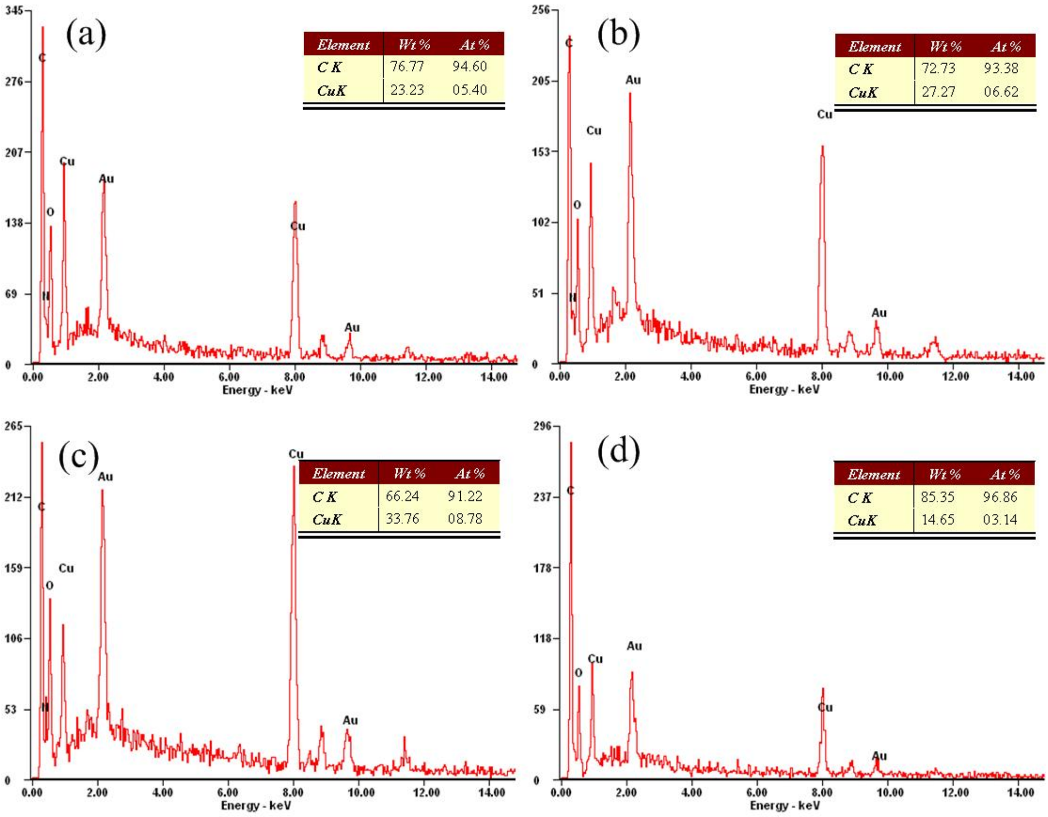

Fig. S5. EDS spectra of the PAN hollow fiber substrates with fixed copper ion; (a), (b), (c), (d) the substrates hydrolyzed by NaOH for 15min, 60min, 120min and 60min follow by acidized with hydrochloric acid.

Tab. S1. The effect of modified conditions on separation performance.

Membrane	H_2 permeance $\times10^{-5}$ mol/(m^2·s·Pa)	CO_2 permeance $\times10^{-5}$ mol/(m^2·s·Pa)	Ideal separation factor
M1	0.347	0.064	5.42
M2	9.63	1.72	5.60
M3	53.6	15.6	3.44
M4	0.922	0.211	4.38
M5	0.038	0.006	5.50

Notes: M1, M2, M3, $Cu_3(BTC)_2$/PAN supported by the PAN hollow fiber substrate hydrolyzed by NaOH for 15min, 60min,120min, respectively; M4, $Cu_3(BTC)_2$/PAN supported by the PAN hollow fiber substrate hydrolyzed for 60min and then acidized by hydrochloric acid; M5, $Cu_3(BTC)_2$ membrane supported by ceramic substrate.

Tab. S2. Mixture gas permeances and separation factors of the $Cu_3(BTC)_2$/PAN HFM at different retentate flux and pressure.

Retentate flow rate (ml/min)	Pressure	Permeate flow rate (ml/min)	Permeance (10^{-5}mol/(m^2·s·Pa))		y_{H2}/y_{CO2}	Separation factor
			H_2	CO_2		
200	0.05	94.07	6.46	1.18	5.46	10.98
	0.1	164.84	5.3	1.39	3.82	10.94
	0.15	272.73	4.89	1.73	2.82	9.91
	0.2	361.26	4.86	2.47	1.97	7.74
	0.25	469.36	4.81	2.81	1.71	7.21
458	0.05	99.64	6.85	1.25	5.50	7.34
	0.1	183.39	6.03	1.42	4.25	7.08
	0.15	291.38	6.02	1.86	3.24	6.58
	0.2	373.44	5.56	2.02	2.75	6.03
	0.25	484.52	5.49	2.38	2.30	5.85
847	0.05	101.22	7.05	1.17	6.01	7.14
	0.1	191.59	6.52	1.26	5.16	7.05
	0.15	298.63	6.51	1.58	4.13	6.29
	0.2	387.10	6.11	1.75	3.48	5.83
	0.25	497.24	6.08	2.00	3.04	5.68

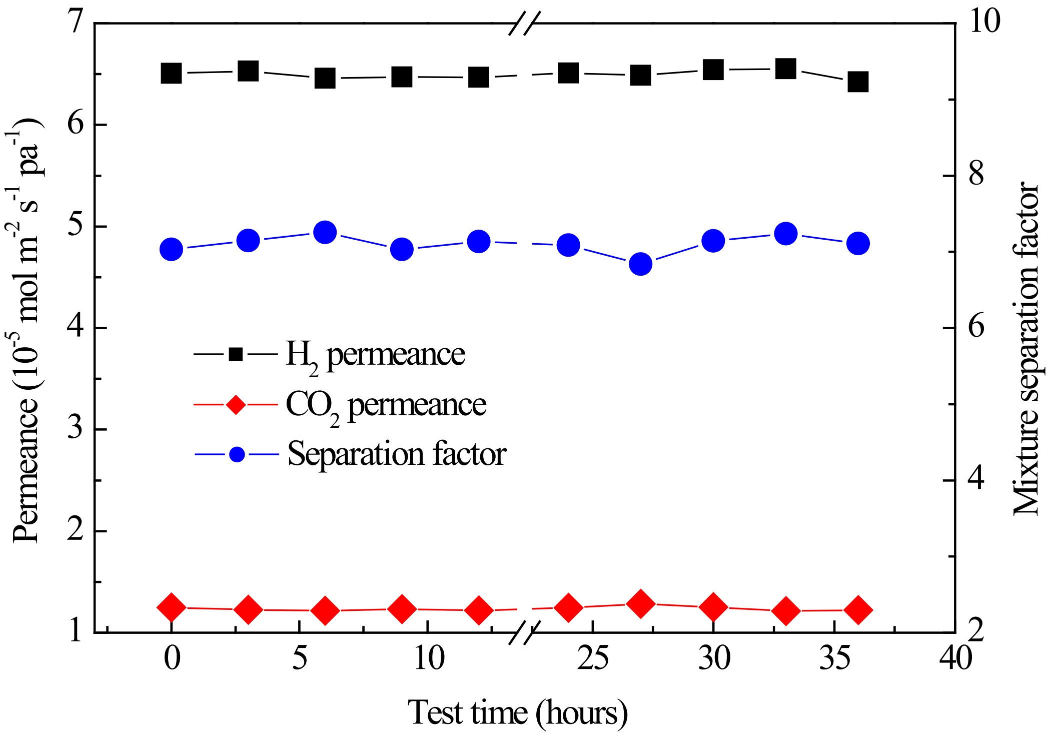

Fig. S6. Mixture gas permeances and separation factor of $Cu_3(BTC)_2$/PAN HFM as function of test time at 0.1 MPa and 20 °C with retentate side flow rate of 847 ml/min.

Tab. S3. Comparison of mixture gas separation performance of the $Cu_3(BTC)_2$/PAN HFM in this study with other membranes in the literature for equimolar H_2/CO_2 mixture.

Membrane	Reference	T(°C)	Pore size (nm)	Separation factor	H_2 permeance ($mol m^{-2} s^{-1} Pa^{-1}$)
zeolite P/NaX	1S	16	0.74	4.50	1.40×10^{-7}
silicate-1	2S	25	0.55	1.84	7.90×10^{-6}
SAPO-34	3S	27	0.38	1.30	3.00×10^{-8}
Matrix $AlPO_4$	4S	35	-	9.70	1.10×10^{-7}
LTA $AlPO_4$	5S	20	0.40	7.60	2.10×10^{-7}
SSZ-13	6S	25	0.38	1.60	3.10×10^{-7}
MFI	7S	450	0.56	17.5	1.86×10^{-7}
MMM ZIF-8	7b	180	-	7.70	6.77×10^{-8}
ZIF-7	8S	200	0.29	6.48	7.71×10^{-8}
ZIF-22	14a	50	0.30	7.20	1.70×10^{-7}
ZIF-78	9S	25	0.38	9.50	0.97×10^{-7}
ZIF-90	10S	200	0.35	7.30	2.37×10^{-7}
ZIF-95	14d	25	0.37	8.48	5.05×10^{-7}
NH2-MIL-53	12c	15	0.75	30.9	1.98×10^{-6}
$Cu_3(BTC)_2$	12a	40	0.90	13.5	4.10×10^{-8}
$Cu_3(BTC)_2$	5b	25	0.90	4.60	6.74×10^{-7}
$Cu_3(BTC)_2$	5c	25	0.90	6.84	1.06×10^{-6}
$Cu_3(BTC)_2$	This work	20	0.90	7.05	6.52×10^{-5}
		40	0.90	11.0	6.45×10^{-5}

Supporting References

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