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

Electronic Supplementary Information (ESI)

Metal based gel as versatile precursor to synthesize stiff and integrated MOF/polymer composite membrane

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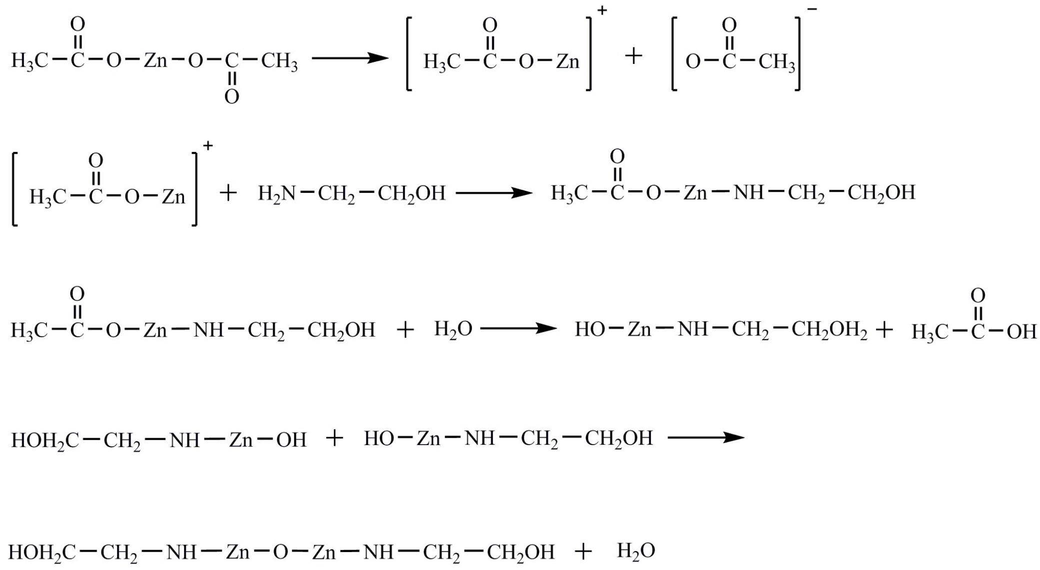
The Reactions

The synthetic reactions of the zinc based gel can be written as follows[S1,2]:



(1)

(2)

(3)

(4)

Note: The water in the step 3 comes from the crystal water in zinc acetate dihydrate.

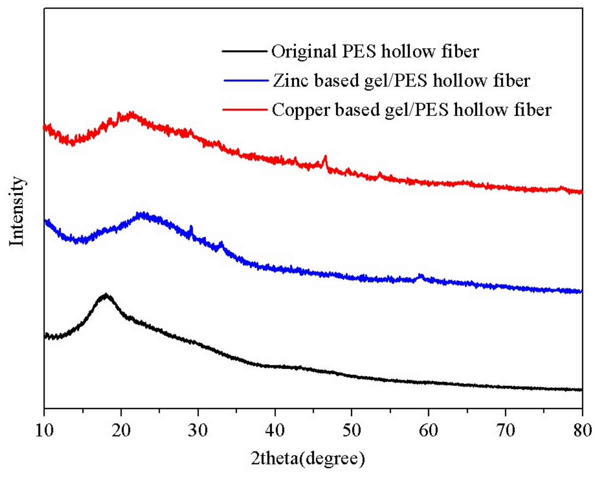


Fig. S1 XRD patterns of the prepared hollow fibers.

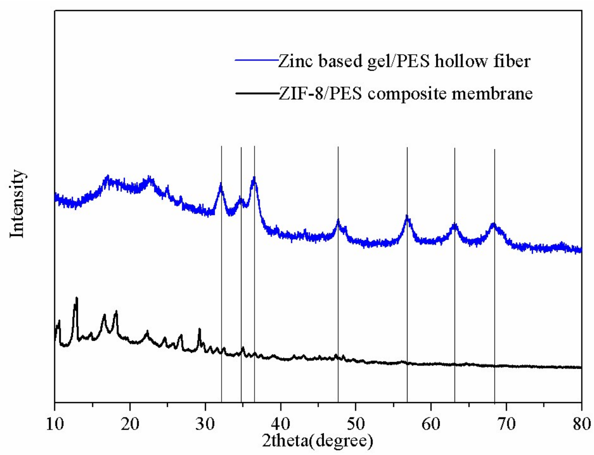


Fig. S2 XRD patterns of the zinc based gel/PES hollow fiber and the ZIF-8/PES composite membrane after the treatment in the oven for 200 ^{o}C and 4 hours.

The zinc based gel/PES hollow fiber and ZIF-8/PES composite membrane were placed in the oven for 200 ^{o}C and 4 hours. The characteristic peaks of zinc oxide appeared obviously in the XRD pattern of zinc based gel/PES hollow fiber after high temperature treatment. However, there was no peak appeared in the ZIF-8/PES composite membrane. This result strongly demonstrated that the metal based gel infiltrated was fully consumed and transformed into ZIF-8 crystals in the solvothermal treatment process.

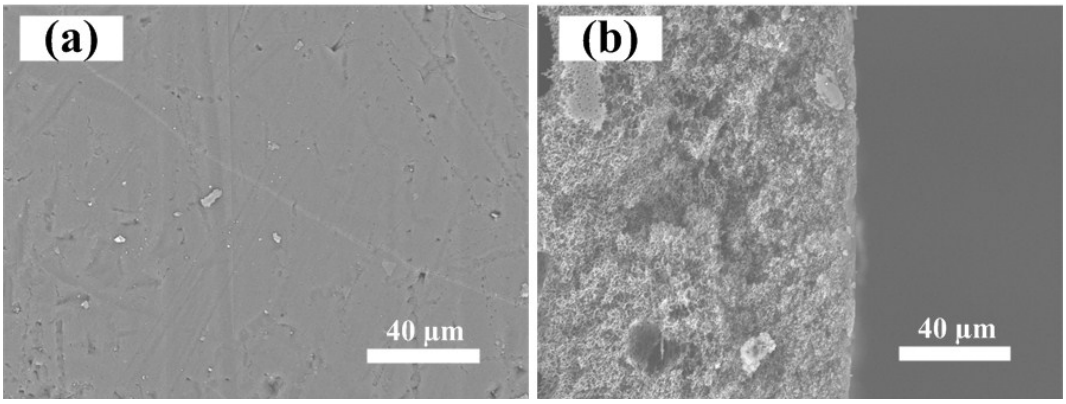


Fig. S3 (a) Top and (b) cross section view SEM images of the original PES hollow fiber.

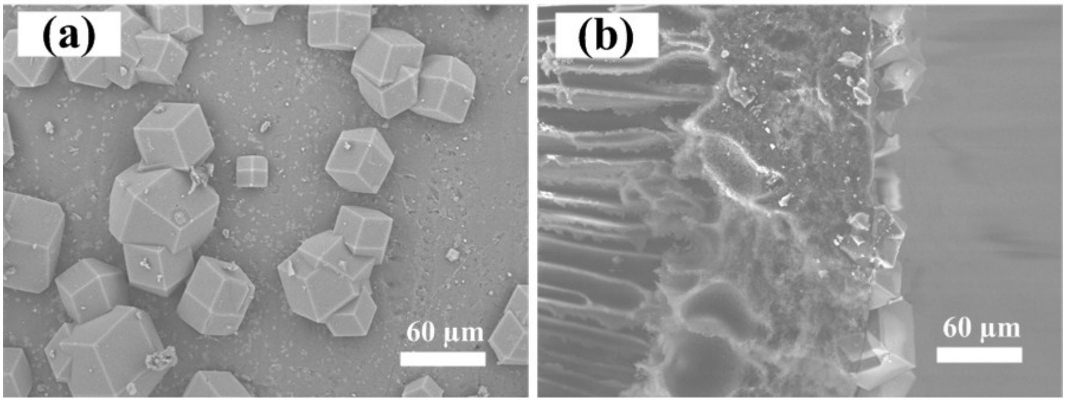


Fig. S4 (a) Top and (b) cross section view SEM images of the ZIF-8 membrane grown on the original PES hollow fiber.

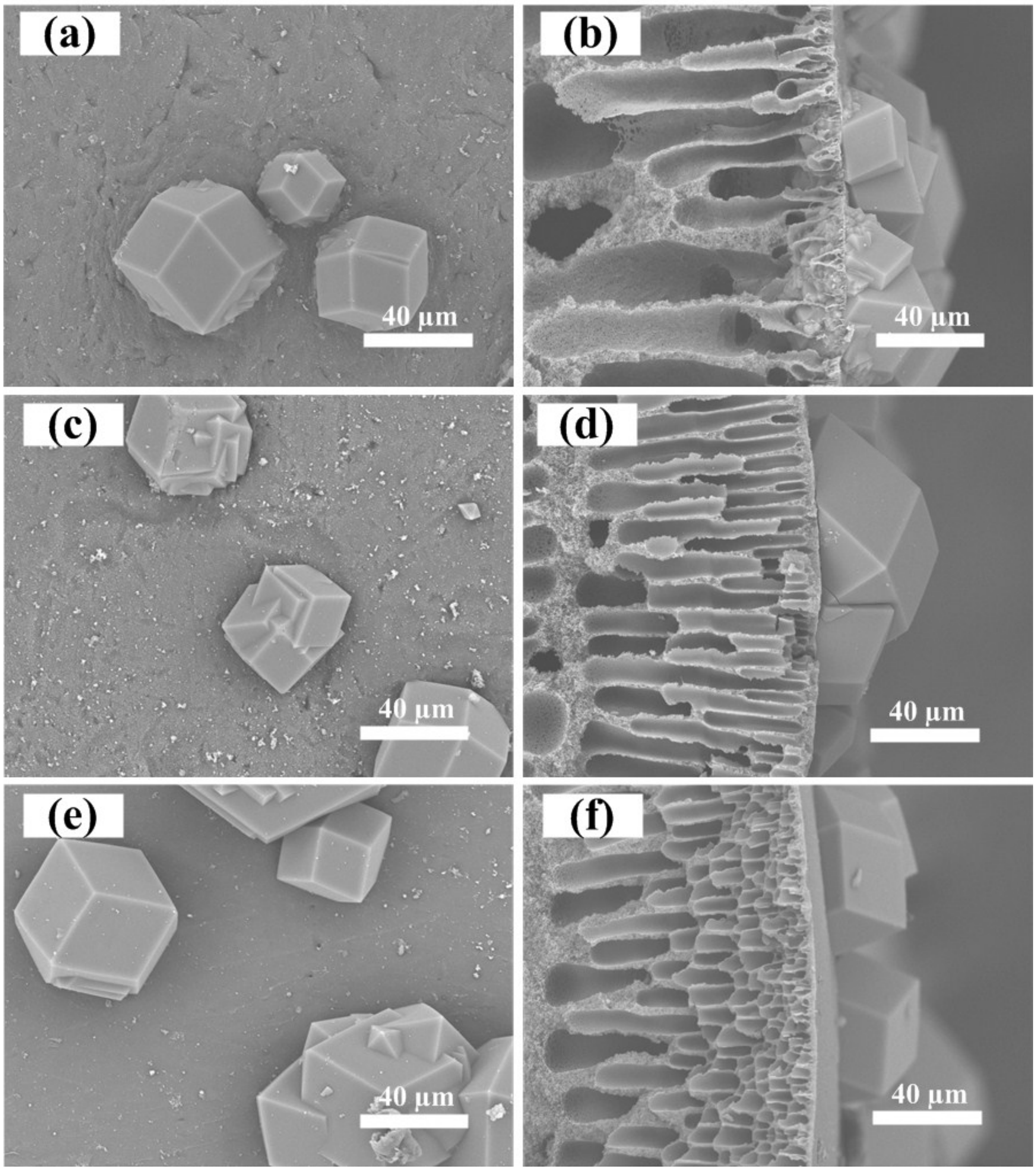


Fig. S5 SEM images of the ZIF-8 membrane grown on the original polymer hollow fiber: (a,b) PVDF, (c,d) PSF and (e,f) PAN.

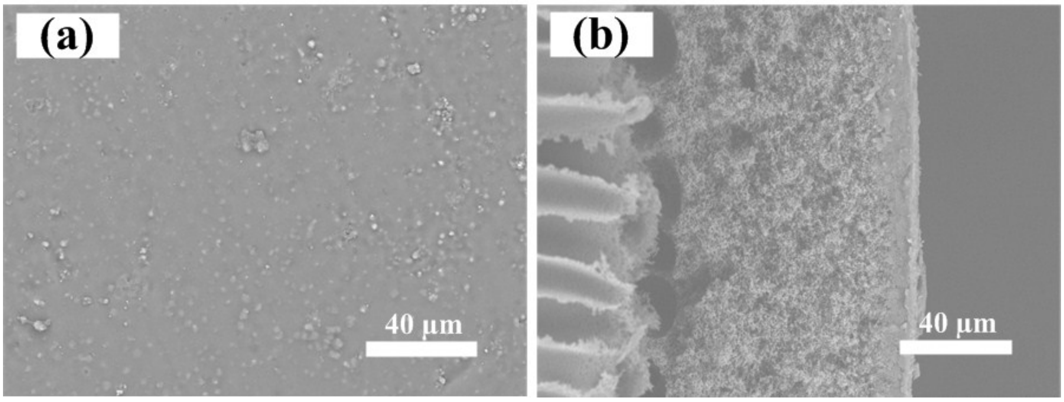


Fig. S6 (a) Top and (b) cross section view SEM images of the copper based gel/PES hollow fiber.

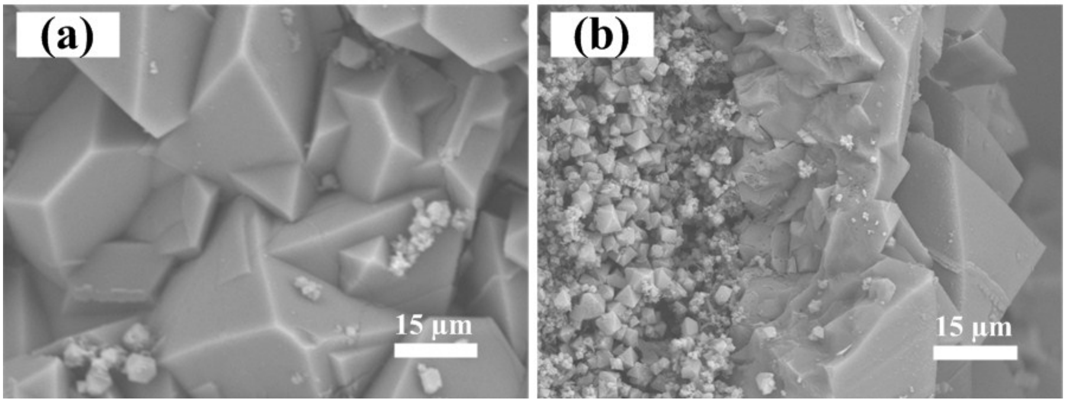


Fig. S7 (a) Top and (b) cross section view SEM images of the $Cu_3(BTC)_2$/PES composite membrane prepared from the copper based gel precursor.

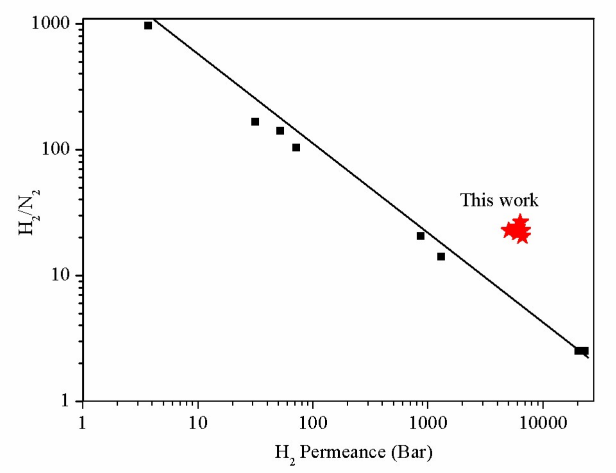


Fig. S8 H_2/N_2 separation performances of the prepared ZIF-8/PES composite membranes.

1 Barrer = 3.348×10^{-16} mol m / (m^2 s Pa). The m is the thickness of the membrane.

Table S1 Gas separation properties of the ZIF-8/PES composite membranes at 20 ºC and 0.05 MPa.

Membrane	Permeance (10^{-9}mol m^{-2} s^{-1} Pa^{-1})				Separation factor		
	H_2	CO_2	O_2	N_2	H_2/CO_2	H_2/O_2	H_2/N_2
M1	111.1	21.2	15.1	4.9	5.2	7.4	22.7
M2	99.4	18.9	13.9	4.1	5.3	7.2	24.2
M3	110.5	22.1	17.8	5.4	5.0	6.2	20.5
M4	106.2	20.9	14.0	4.0	5.1	7.6	26.6
M5	84.4	15.5	10.7	3.7	5.4	7.9	22.8
M6	100.6	19.2	13.9	4.6	5.2	7.2	21.9
M7	111.8	21.4	15.5	5.0	5.2	7.2	22.4

Note: M1, M2, M3, M4, M5, M6 and M7 represent the prepared ZIF-8/PES composite membranes.

Table S2 Comparison of gas separation performance of the ZIF-8/PES composite membrane in this work with other polymer supported MOF membranes in the literature.

Membrane	Substrate	Pore size (nm)	Temperature(°C)	H_2 Permeance (mol m^{-2} s^{-1} Pa^{-1})	Separation factor		Reference
					H_2/CO_2	H_2/N_2	
ZIF-7	PVDF	0.29	25	2.35×10^{-6}	18.43	20.27	26
ZIF-7	PVDF	0.29	25	1.33×10^{-6}	16.32	18.30	43
ZIF-7	PSF	0.29	35	2.20×10^{-9}	2.4	35.1	S3
ZIF-8	PSF	0.34	35	4.70×10^{-9}	2.6	18.3	S3
ZIF-8	PSF	0.34	35	2.00×10^{-7}	-	12.4	S4
ZIF-8	Polyester	0.34	25	1.60×10^{-6}	-	-	S5
ZIF-8	Nylon	0.34	25	1.97×10^{-6}	-	4.3	S6
ZIF-8	Nylon	0.34	20	1.13×10^{-6}	-	4.6	S7
ZIF-8	PVDF	0.34	25	2.01×10^{-6}	16.3	18.1	26
ZIF-8	PVDF	0.34	25	2.44×10^{-6}	12.18	14.31	43
ZIF-8	PAN	0.34	20	3.05×10^{-7}	6.85	-	28
ZIF-8	Torlon	0.34	25	1.84×10^{-7}	-	-	S8
ZIF-8	PES	0.34	60	4.00×10^{-7}	-	9.9	46b
ZIF-90	Torlon	0.35	35	1.92×10^{-7}	1.8	6.3	25
$Cu_3(BTC)_2$	PSF	0.90	25	4.85×10^{-7}	21.03	2.90	S9
$Cu_3(BTC)_2$	PSF	0.90	25	7.90×10^{-8}	7.2	-	S10
$Cu_3(BTC)_2$	PAN	0.90	20	9.63×10^{-5}	5.6	4.85	28
$Cu_3(BTC)_2$	PVDF	0.90	25	8.46×10^{-6}	7.30	5.87	43
$Cu_3(BTC)_2$	PVDF	0.90	25	2.01×10^{-6}	8.1	6.5	S11
ZIF-8	PES	0.34	20	1.11×10^{-7}	5.2	22.7	This work

Table S3 Gas separation properties of the ZIF-8/PVDF, ZIF-8/PSF, ZIF-8/PAN and $Cu_3(BTC)_2$/PES composite membranes at 20 ºC.

Membrane	Substrate	Permeance (mol m^{-2} s^{-1} Pa^{-1})		Separation factor
		H_2	N_2	H_2/N_2
ZIF-8/PVDF	PVDF	8.66×10^{-7}	9.77×10^{-8}	8.9
ZIF-8/PSF	PSF	2.29×10^{-7}	1.24×10^{-8}	18.5
ZIF-8/PAN	PAN	1.03×10^{-8}	8.52×10^{-10}	12.1
$Cu_3(BTC)_2$/PES	PES	3.43×10^{-6}	5.62×10^{-7}	6.1

The larger H_2 permeance of $Cu_3(BTC)_2$/PES composite membrane was attributed to the larger pore size of the $Cu_3(BTC)_2$. The lower H_2 permeance of ZIF-8/PAN composite membrane was caused by the thicker ZIF-8 layer and the pore shrinkage from cyclization and crosslinking reaction of PAN molecules in the high temperature.[S12] Compared with the ZIF-8/PSF membrane, the relatively higher H_2 permeance of ZIF-8/PVDF composite membrane was resulted from the large pore size of PVDF microfiltration hollow fiber.

Table S4 The mixture gas permeances and selectivities of the ZIF-8/PES composite membrane (M7).

$Gas_{i/j}$	Knudsen constant	Permeance (mol m^{-2} s^{-1} Pa^{-1})		Mixture separation factor
		i	j	
H_2/CO_2	4.7	9.11×10^{-8}	1.82×10^{-8}	5.0
H_2/O_2	4.0	9.22×10^{-8}	1.34×10^{-8}	6.9
H_2/N_2	3.7	9.29×10^{-8}	4.56×10^{-9}	20.4

Supporting References

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