Supporting Information

A simple and scalable method for preparing low-defect ZIF-8 tubular membranes

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1. Experimental details

1.1 Materials and reagents:

The commercial porous α-alumina tubes were purchased from Hyflux Ltd. Co. and Pall Ltd. Co. The tubes were cut into 60 mm and 75 mm in length respectively and washed sequentially with distilled water and ethanol under ultrasonication for several times to remove impurities and dried for 5 h at 373 K, then calcined for 6 h at 823 K.

Chemicals used in membrane synthesis include zinc chloride (≥98 %), zinc acetate (98.0 %), sodium formate dihydrate (≥99.5 %), ethylene glycol monomethyl ether ($C_3H_8O_2$, EGME, 99.0 %), monoethanolamine (C_2H_7NO, MEA, 99.0 %) and methanol anhydrous (≥99.5 %) purchased from Sinopharm Chemical Reagent Co., Ltd. 2-methylimidazole (Hmim, 99 %) was supplied by Sigma-Aldrich Chemical. Co. Ltd.

1.2 ZIF-8 membrane synthesis

ZnO coating sol: A ZnO sol was prepared as follows: 8.34 g $Zn(Ac)_2$ was dissolved in 48ml EGME under stirring at 343 K. Then 2.4ml MEA was added dropwise into the solution. Finally the sol was aged at room temperature for around 10 h to obtain a EGME sol contaning

14.3 wt % zinc for ZnO coating [1, 2]. The internal surface of the cleaned tube was coated with the above zinc sol by a slip-casting technique, followed by drying at 373 K for 1 h. This procedure was repeated for two times to get a continuous sol layer. Then the tube was calcined at 673 K in air with a heating rate of 1 $K \cdot min^{-1}$ for 2 h. Finally, the tubes with a thin layer of ZnO coating of around 0.5μm could be achieved for membrane growth.

ZIF-8 membrane formation: The tube with ZnO layer was wrapped with Teflon tape to avoid ZIF-8 deposition on the outer surface before it was placed in a synthesis solution. Firstly, the tube with ZnO layer was placed in a 0.5 M Hmim methanol solution at 323 K for 2.5 h to activate the coating surface and produce nucleation sites. Secondly, the activated tube was transferred to another synthesis solution with a molar composition of 0.65 HCOONa : 1.0 $ZnCl_2$: 1.5 Hmim : 450 MeOH at 373 K for 5 h for membrane growth [3, 4]. The typical synthesis solution was prepared by dissolving in turn 1.0780 g zinc chloride, 0.9720 g 2-methylimidazole and 0.5400 g sodium formate in 80 ml methanol under stirring for 20 min before being transferred to a 100 mL Teflon stainless-steel autoclave. After the solvothermal reaction at 373 K for 5 h, the as-synthesized membrane was taken out, naturally cooled to room temperature and thoroughly washed with methanol to remove some residues. Finally, the membrane was dried at 303 K for 24 h and then stored in a desiccator for later use. Prior to testing gas permeation, two ends of the tube were sealed with epoxy resin glue. By using a brush, a thin and uniform layer of the glue material was applied to both ends (5 mm) of the tube. Then, it was dried overnight at room temperature. After the sealing, the tube was treated under vacuum at 323 K for 12 h to test gas permeation.

2. Sample characterization

X-ray diffraction (XRD) measurements were performed on a D/max-2400 X-ray diffractometer using Cu *Kα* radiation in the range of 3-100º operating at 20 kV/100 mA.

Scanning electron microscopy (SEM) images were inspected with a NOVA NANOSEM 450 SEM (FEI company). The working parameters of the SEM are as follows: high voltage (HV) 5-

15 kV, work distance (WD) 5-10 mm and Spot size 3.0. Another SEM is Quanta 200 with the oparation parameters of 20~30 kV.

TOF-SIMS measurement were analyzed by an ION-TOF GmbH TOF-SIMS V spectrometer equipped with 25 keV Bi^{3+} cluster ion source that has an average pulsed current of 0.1 pA. Spectra were obtained and averaged over three 200 × 200 μm^2 areas. Each spectrum was collected for 40 s at ion flux dosage of less than 2×10^{11} ions/cm^2.

TG measurements were performed simultaneously on a Netzsch STA 449 C thermoanalyzer. For this purpose, ca. 1.2 mg of material was filled into alumina crucibles and heated in a flow of air with a ramp of 5 K/min from 303 K up to 873 K.

The gas permeation properties of the ZIF-8 membrane were evaluated using single gases of H_2 (0.29 nm), CO_2 (0.33 nm), N_2 (0.36 nm), CH_4 (0.38 nm), C_3H_8 (0.43 nm), C_4H_{10} (0.48 nm), and SF_6 (0.51 nm) in a permeation set up as shown in Fig. S1. The membrane was placed in a home-made stainless steel module with a cylindrical geometry. The feed stream was pressurized, while downstream pressure was maintained at atmospheric pressure. The pressure difference through the membrane was tested at 0.1 MPa. The gas flux was measured by a soap film bubble flow meter. Before the measurement of each gas species (except for H_2), the membrane permeation system was swept with H_2 to desorb the trapped gas molecules in the ZIF-8 pores. The permeance, P_i, is defined as:

$$P_i = \frac{N_i}{\Delta P_i \, A}$$

where N_i is the permeate rate of component i (mol·s^{-1}), ΔP_i the trans-membrane pressure difference of i (Pa), and A is the membrane area (m^2). The ideal separation factor is calculated as the ratio of permeance P_i and P_j.

$$\alpha_{i/j} = \frac{P_i}{P_j}$$

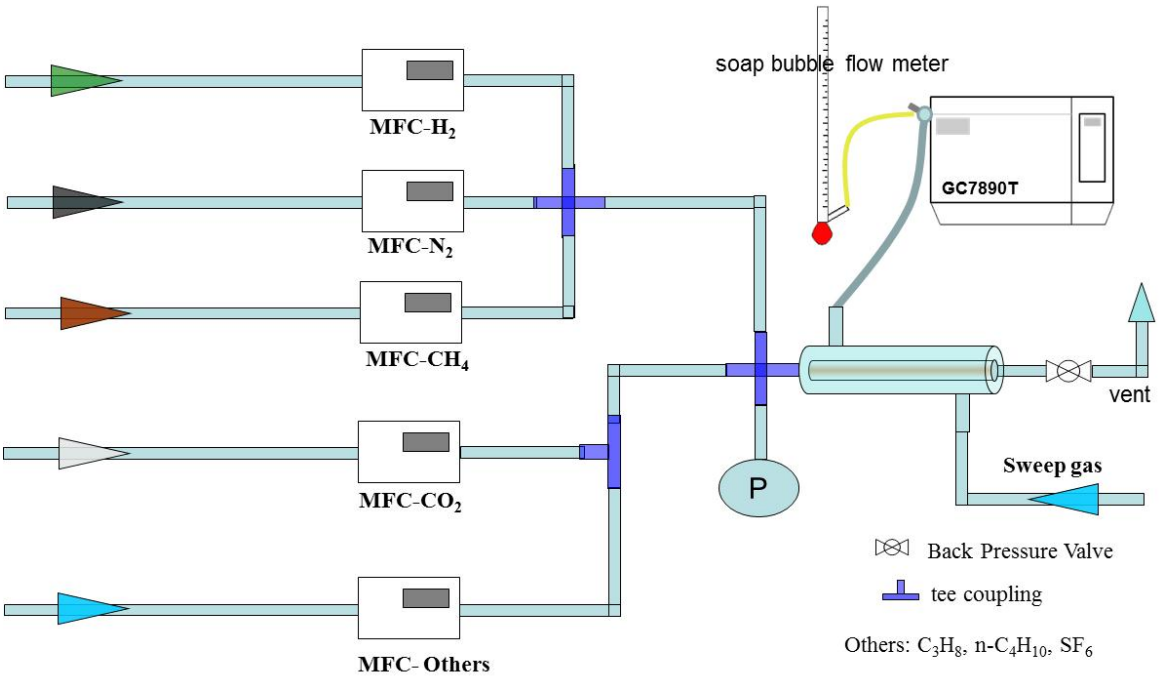

Fig. S1 Schematic diagram of the gas permeation apparatus

3. Result and discussion

(1) Porous α-alumina tubes as supports

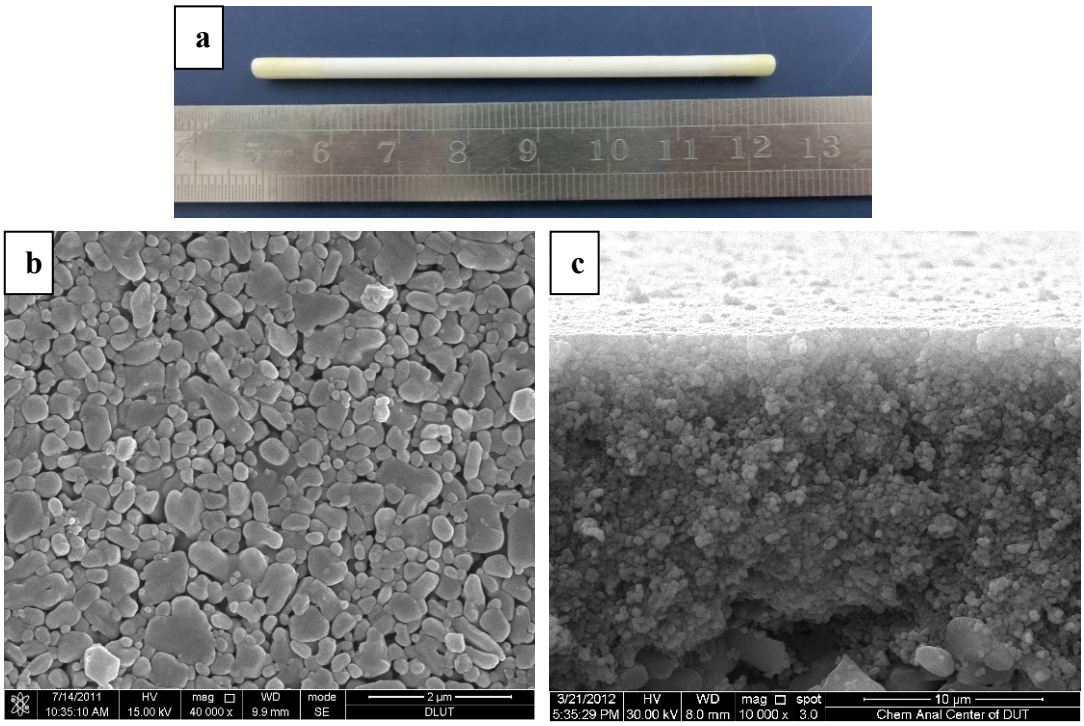

Fig. S2 Photo and SEM images of the HFT support:

a: HFT; b: Top view; c: Cross-section view

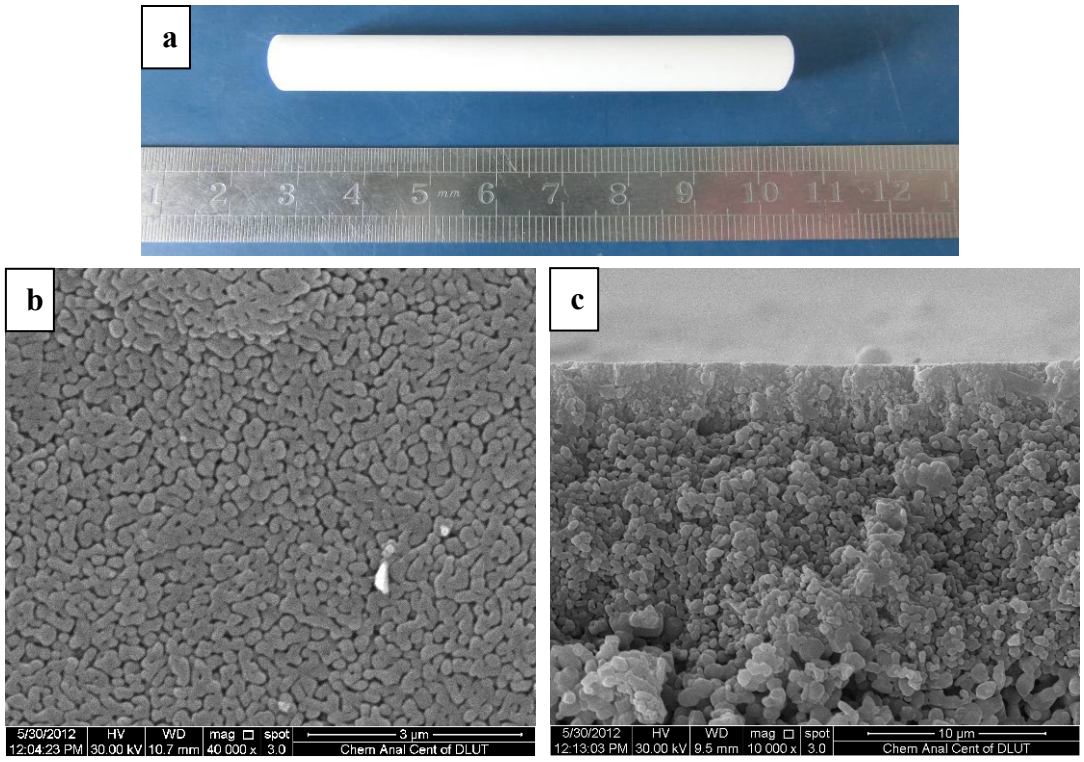

Fig. S3 Photo and SEM images of the UHFT support:

a: UHFT; b: Top view; c: Cross-section view

(2) The tubes coated with a contaning ZnO sol

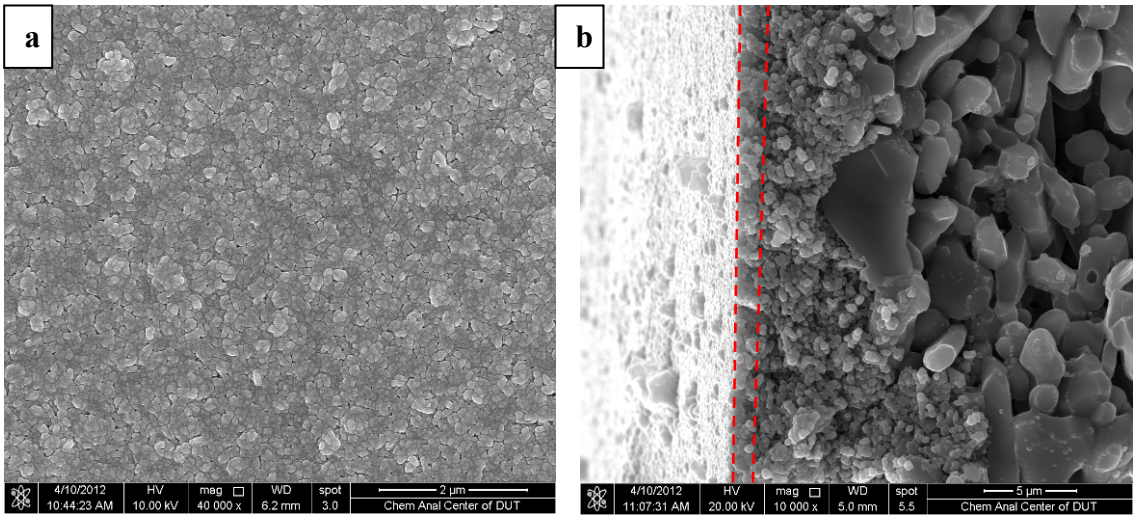

Fig. S4 SEM images of the tube coated with the sol:

a: Top view; b: Cross-section view

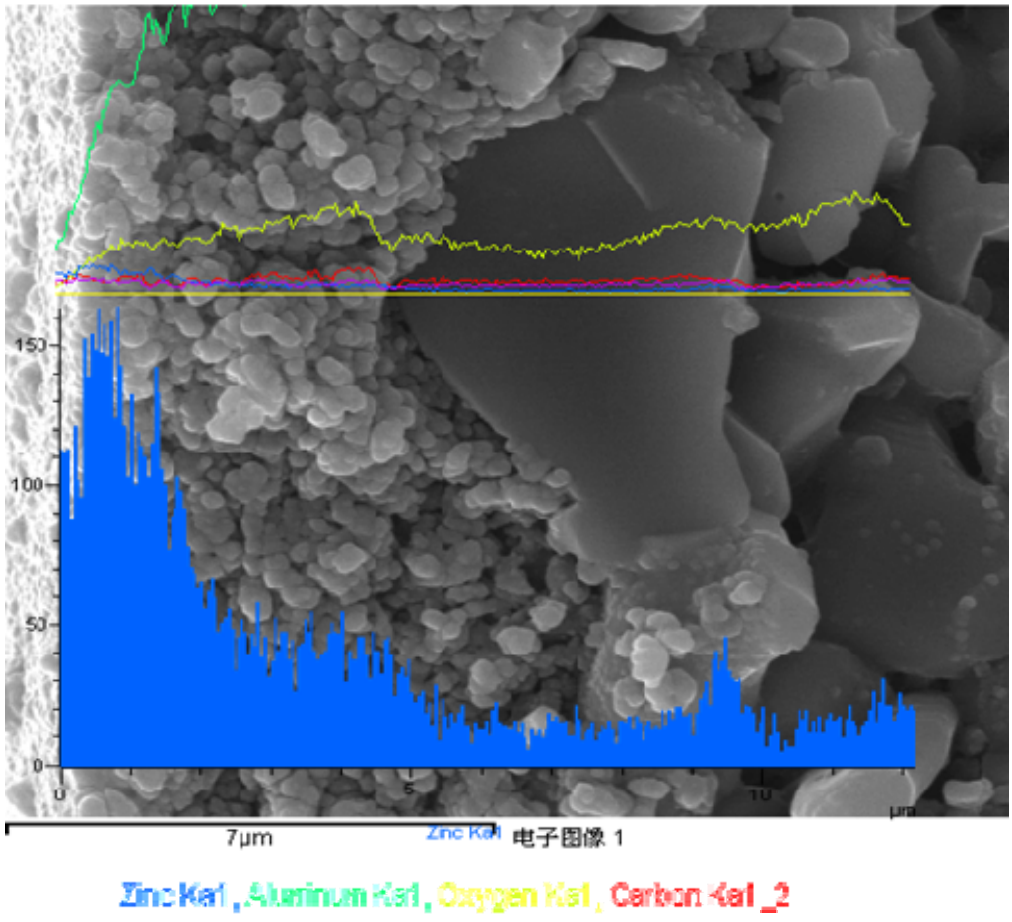

Fig. S5 Energy-dispersive X-ray spectroscopy (EDXS) of the tube's cross section after coating with the sol.

(3) Surface of the tubes with an ultrathin ZnO layer after activation

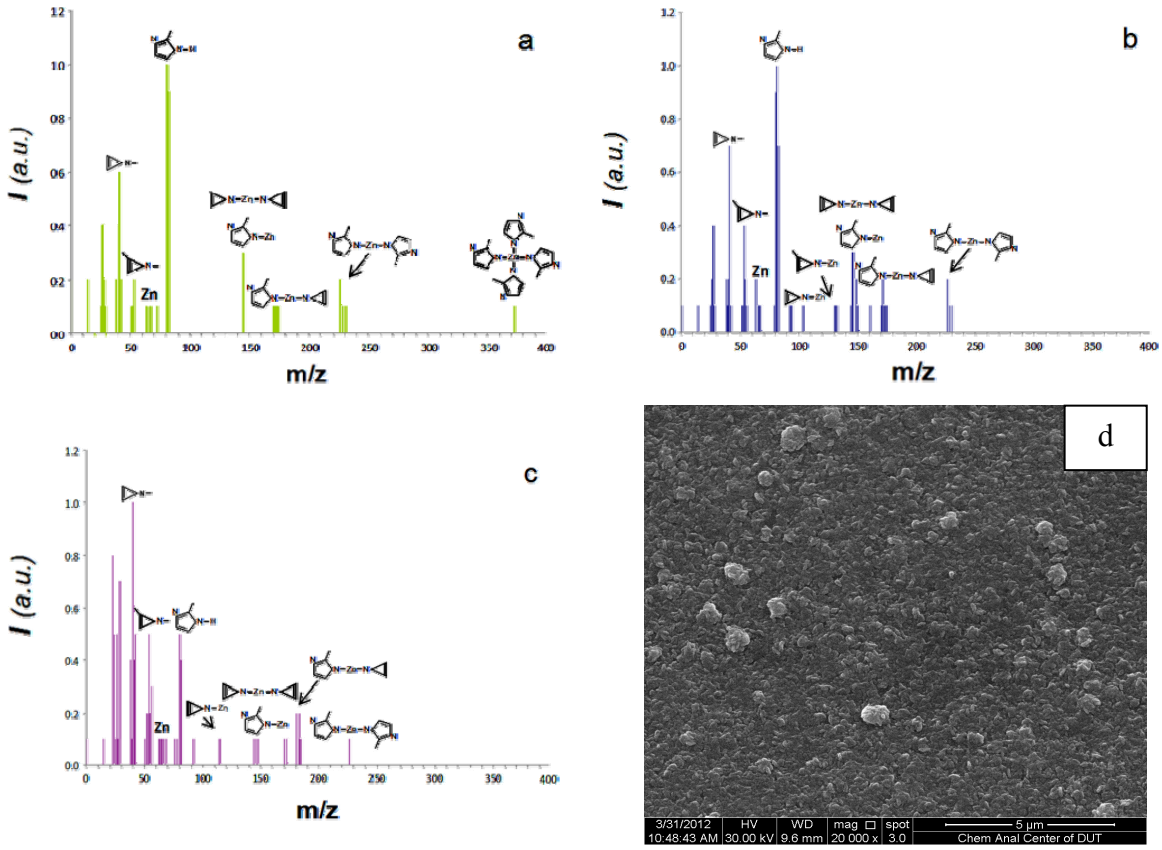

Fig. S6 ToF-SIMS spectra of the ZnO layer activated with Hmim (a), ZIF-8 nanoparticle (b), and ZIF-8 membrane (c) and (d) SEM image of the tube with a ZnO layer after activation.

(4) ZIF-8 membrane formed on the tubes coated with a ZnO layer

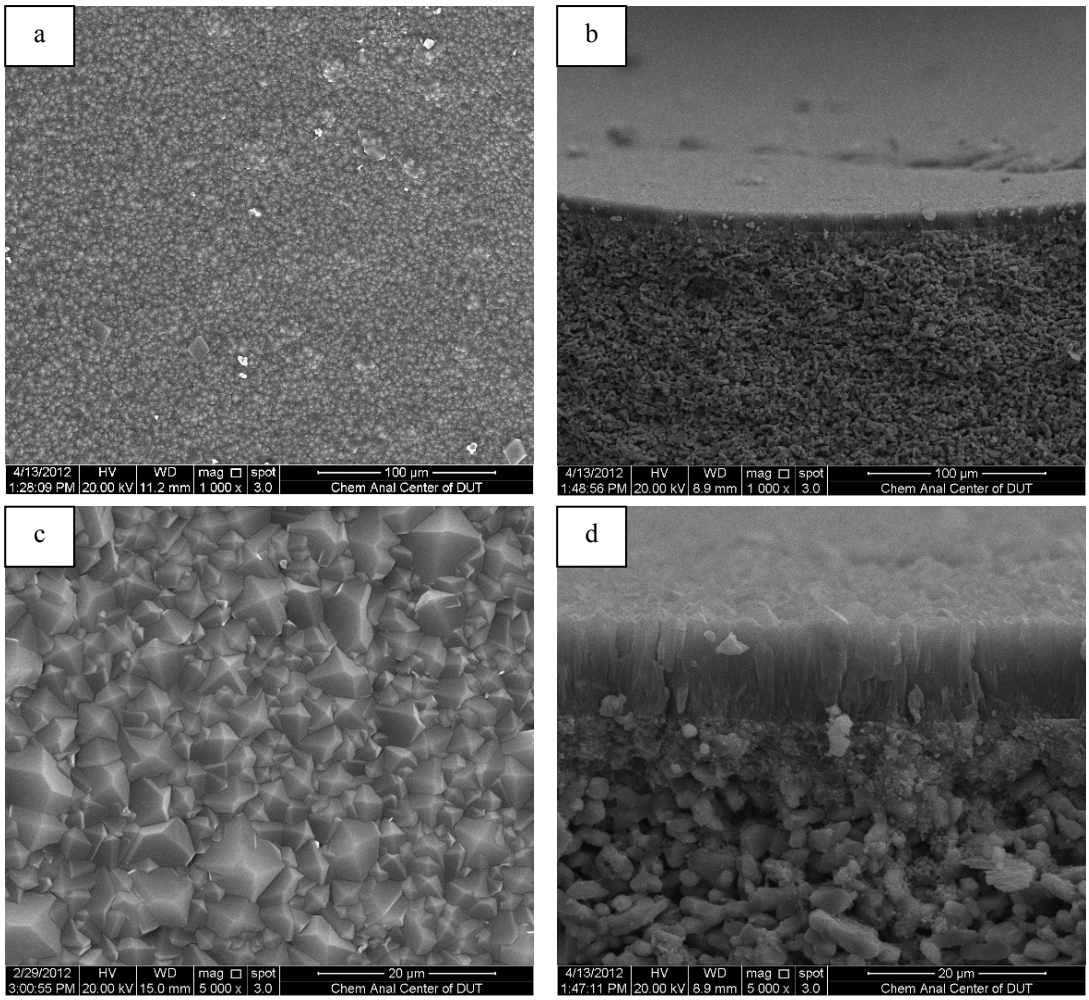

Fig. S7 SEM images of the tube with a ZnO layer after membrane growth

a, c: Top view; b, d: Cross-section view; c, d: High magnification of a, b

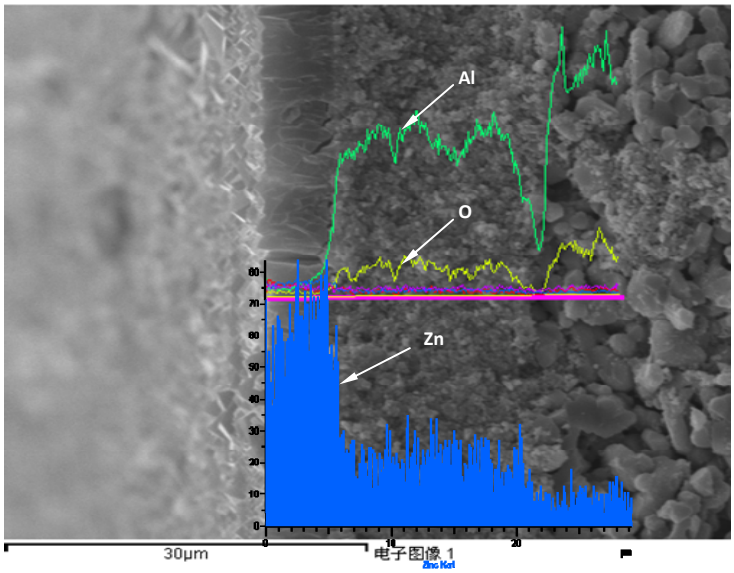

Fig. S8 Energy-dispersive X-ray spectroscopy (EDXS) of the membrane grown on tube coated with ZnO, showing the intermediate Zn element is higher than the membrane and the supporting.

(5) The membrane grown on the tube without ZnO coating

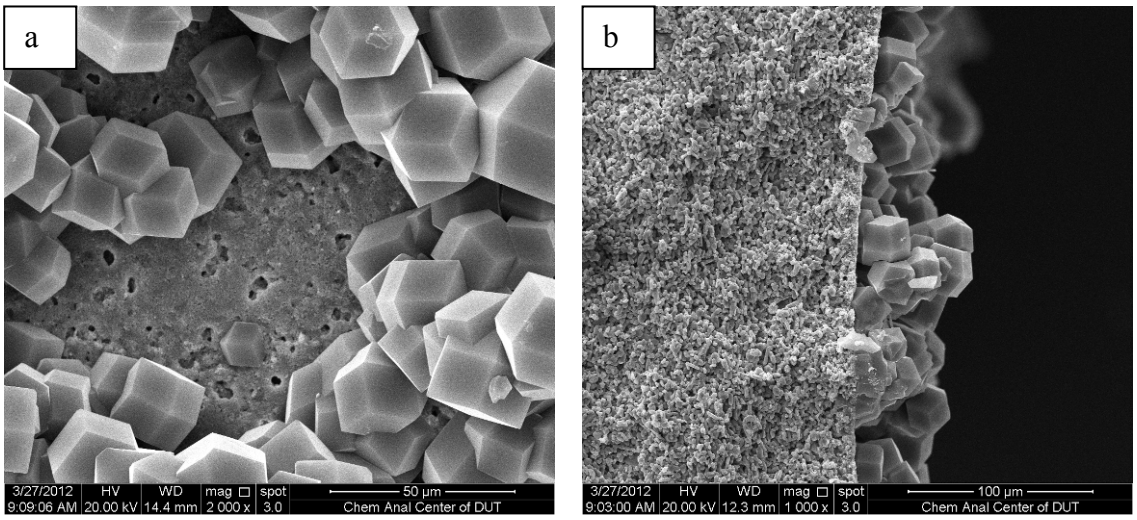

Fig. S9 SEM images of the membrane grown on the tube without ZnO layer. a: Top view and b: Cross-section view.

(6) The membrane grown on the tube with ZnO coating without activation

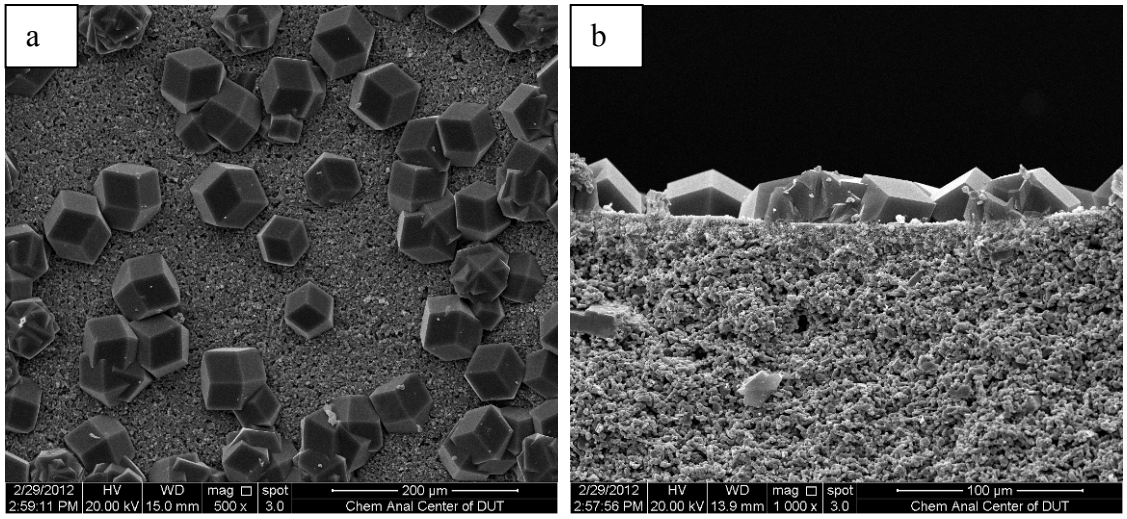

Fig. S10 SEM images of the membrane grown on the tube with ZnO coating without activation: a: Top view; b: Cross section;

(7) XRD anylysis of the samples

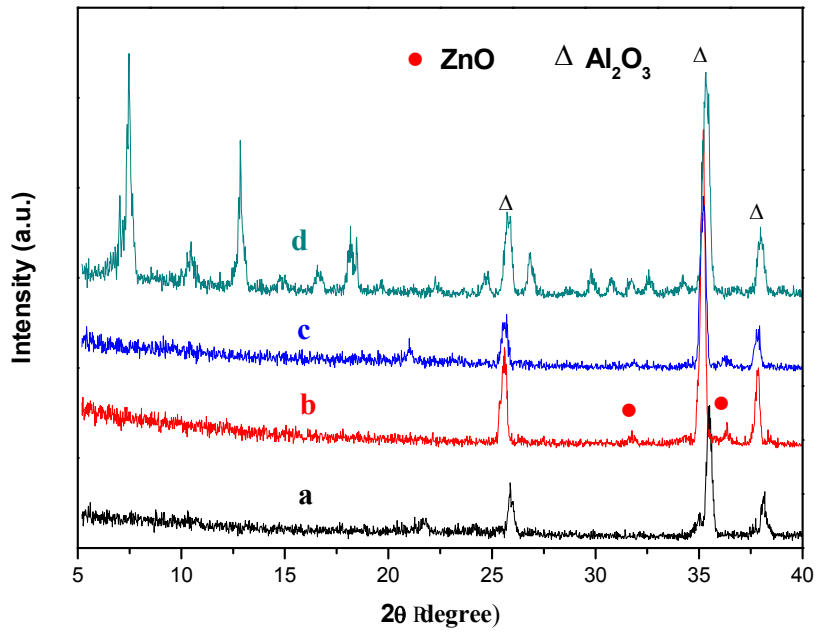

Fig. S11 XRD patterns of the substrate and membrane

a: Alumina tube; b: Alumina tube with ZnO coating;

c: Alumina tube with ZnO coating after activation; d: the membrane

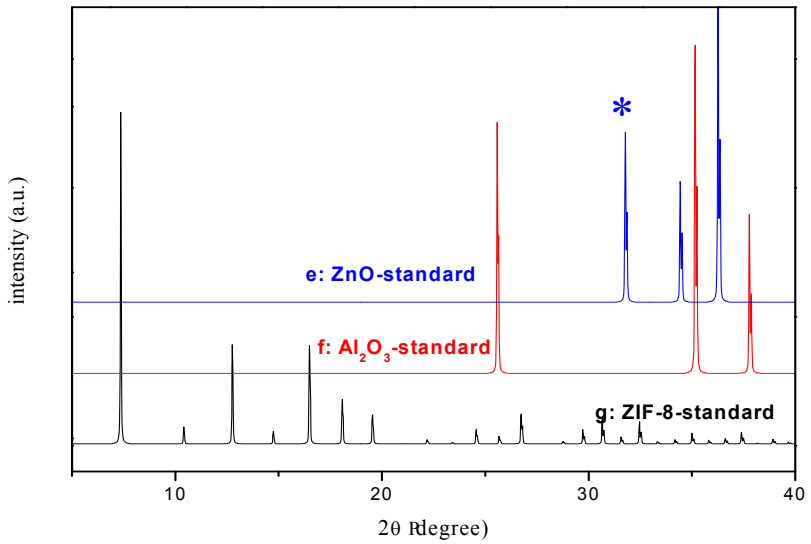

Fig. S12 XRD patterns of different simulated samples

It is clearly seen that after the treatmeat by Hmim methnol solution, there is no ZIF-8 peak on the surface of the support modified with ZnO layer.

(8) TGA analysis of ZIF-8 powders

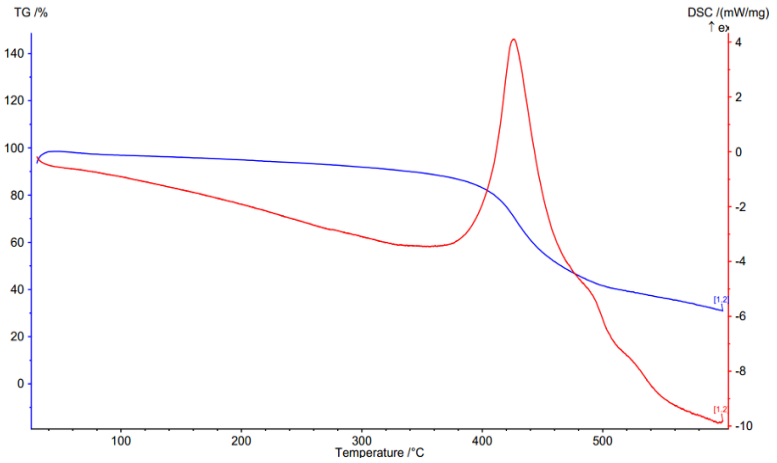

Fig. S13 TGA curve of ZIF-8 powders obtained from the membrane synthesis

(9) ZIF-8 membrane grown on the Zinc foil dealed with H_2O_2

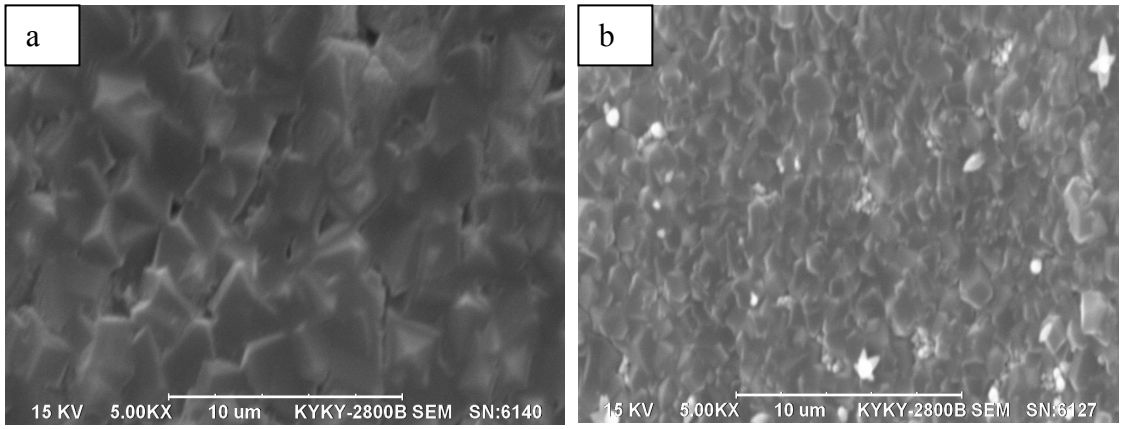

Fig. S14 SEM of (a) ZIF-8 membrane grown the Zinc foil treated with H_2O_2 and (b) the surface of Zinc foil treated with H_2O_2

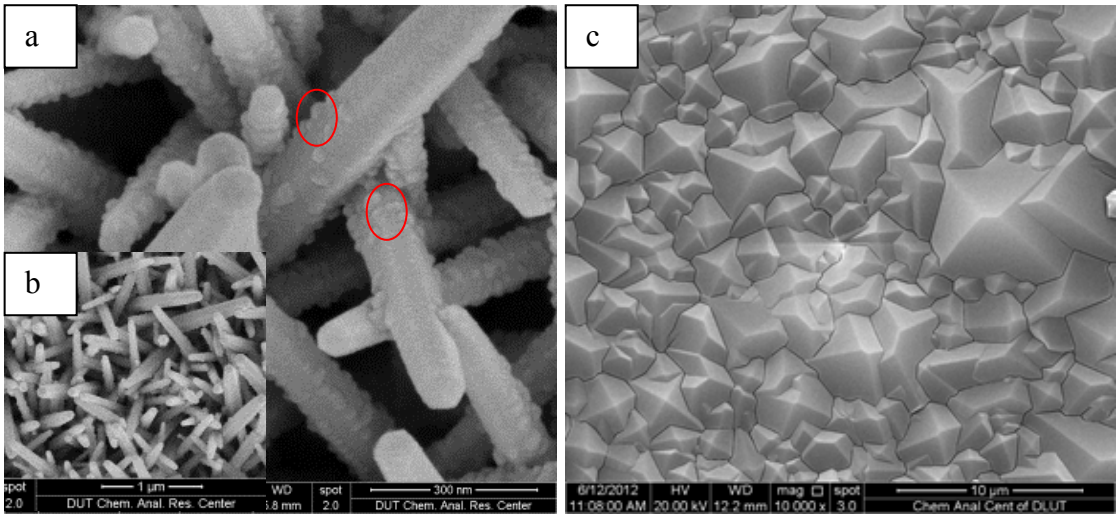

Fig. S15 SEM images of the samples from the ZnO rods (a, b) activated with Hmim methanol solution at 323K for 2.5 h and ZIF-8 membrane grown on it (c)

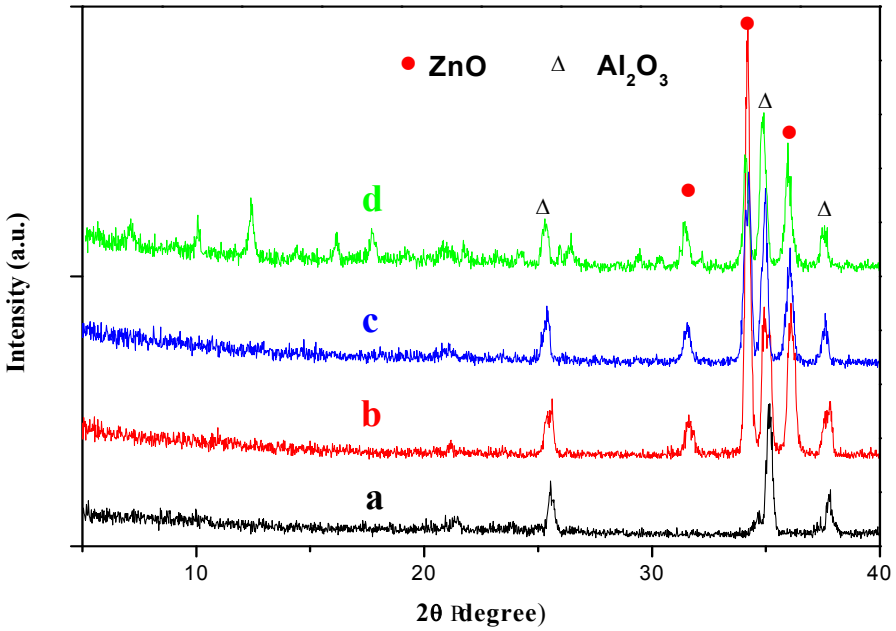

Fig. S16 XRD patterns of the samples; a: Alumina disc; b: Alumina disc with ZnO rods; c: Alumina disc with ZnO rods after activation with Hmim methanol solution at 323 K for 2.5 h; d: ZIF-8 layer grown on the disc with rods after activation.

(10) Single gas permeation test

Permeances for the bare hollow fiber tube and tube coated with ZnO layer

It is from the Fig. S14 seen that after the treatment, the gas permeance of the modified tube is slightly lower than that of the bare one.

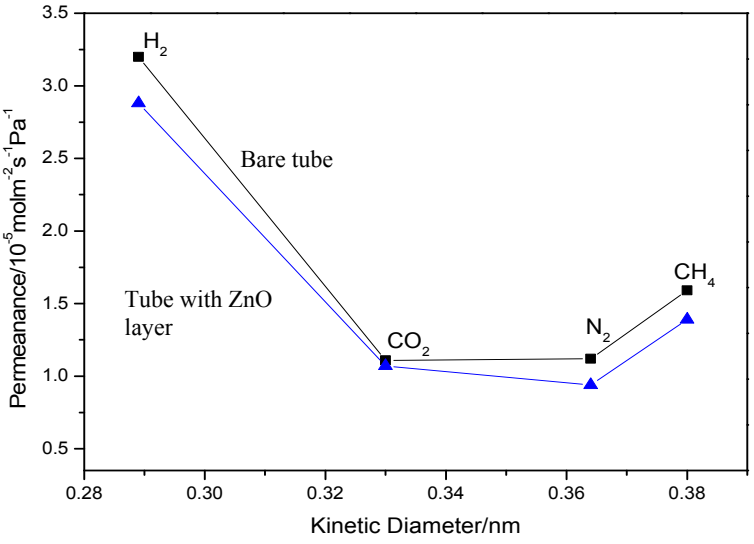

Fig. S17 Single gas permeances through the bare HFT substrate and tube coated with an ultrathin ZnO layer

***Table* S1 Results of single component permeation through three ZIF-8 membranes supported on HFT tubes with 30 mm in length prepared in parallel batches.[a]**

Membr. code	Permeance/10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1}			Permselectivity	
	H_2	N_2	CO_2	H_2/N_2	H_2/CO_2
SM1	99.8	9.2	19.3	10.9	5.2
SM2	66.5	6.0	11.4	11.0	5.8
SM3	60.9	6.3	11.8	9.6	5.2

[a] Permeation performed at 298 K and 0.1 MPa.

Permeation test for the six membranes on the 60 mm long HFT supports obtained from one batch synthesis by this new method under the same condition.

In one batch synthesis, six ZIF-8 membranes on HFT supports with 60 mm in length were obtained and their permeation properties were tested as shown in Table S2 to S3.

Table S2 Permeances through the six ZIF-8 membranes on the HFT substrates with 60 mm in length at 298 K and 0.1 MPa

Membr. code	Permeance (×10^{-8}mol·m^{-2}·s^{-1}·Pa^{-1})				
	H_2	CO_2	N_2	CH_4	SF_6
M1	72.7	14.2	8.98	9.22	0.36
M2	83.5	17.2	11.5	12.0	0.49
M3	61.8	12.0	7.7	7.68	0.38
M4	88.9	26.8	15.3	15.4	1.13
M5	61.3	11.0	7.56	7.74	0.32
M6	65.2	13.5	8.02	8.31	0.39

Table S3 Ideal selectivities through the six ZIF-8 membranes on the HFT substrates with 60 mm in length at 298 K and 0.1 MPa

Membr. code	Permselectivity			
	H_2/CO_2	H_2/N_2	H_2/CH_4	H_2/SF_6
M1	5.1	8.1	7.9	201.7
M2	4.8	7.3	6.9	168.8
M3	5.1	8.0	8.0	161.5
M4	3.3	5.8	5.8	78.5
M5	5.6	8.1	7.9	192.1
M6	5.6	8.1	7.8	164.5

Single gas permeation through the ZIF-8 membranes **on the 75 mm long HFT and UHFT supports** ***by this new method under the same condition as shown in Table S4 to S7.***

Table S4 Single gas permeances through the ZIF-8 membranes on the HFT substrates with 75 mm in length at 298 K and 0.1 MPa except for the permeance of *n*-C_4H_{10} at 0.05 MPa.

Membrane No.	Permeance ($\times10^{-8}$mol·m^{-2}·s^{-1}·Pa^{-1})						
	H_2	CO_2	N_2	CH_4	C_3H_8	n-C_4H_{10}	SF_6
HFM1	97.4	26.5	12.3	12.9	3.7	1.0	0.89
HFM2	68.6	14.4	9.7	10.0	1.8	0.9	0.38
HFM3	63.9	12.2	7.8	7.9	0.9	0.6	0.30

Table S5 Ideal separation factor through the ZIF-8 membranes on the HFT substrates with 75 mm in length at 298 K and 0.1 MPa except for the permeance of *n*-C_4H_{10} at 0.05 MPa.

Membrane No.	Permselectivity					
	H_2/CO_2	H_2/N_2	H_2/CH_4	H_2/C_3H_8	H_2/n-C_4H_{10}	H_2/SF_6
HFM1	3.7	7.9	7.5	26.3	96.5	109.5
HFM2	4.8	7.0	6.8	38.1	72.9	180.4
HFM3	5.2	8.2	8.1	68.7	106.6	213.1

Table S6 Single gas permeances through the ZIF-8 membranes on the UHFT substrates at 298 K and 0.1 MPa except for the permeance of *n*-C_4H_{10} at 0.05 MPa.

Membrane No.	Permeance ($\times10^{-8}$mol·m^{-2}·s^{-1}·Pa^{-1})						
	H_2	CO_2	N_2	CH_4	C_3H_8	n-C_4H_{10}	SF_6
UHFM1	20.8	5.12	2.02	2.00	0.139	0.106	0.07398
UHFM2	19.8	4.69	2.05	2.06	0.130	0.115	0.0764

Table S7 Ideal selectivities through the ZIF-8 membranes on the UHFT substrates at 298 K and 0.1 MPa except for the permeance of *n*-C_4H_{10} at 0.05 MPa.

Membrane No.	Permselectivity					
	H_2/CO_2	H_2/N_2	H_2/CH_4	H_2/C_3H_8	H_2/n-C_4H_{10}	H_2/SF_6
UHFM1	4.1	10.3	10.4	149.6	195.7	281.5
UHFM2	4.7	9.6	9.6	151.4	172.2	258.6

HFM represents the ZIF-8 membrane on the HFT substrate;

UHFM represents the ZIF-8 membrane on the UHFT substrate.

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Table S8 Comparison of single gas permeances between the MOF membranes prepared in this work and the membranes from the literatures

Membranes	Support shape	pore size /nm	Area /cm^2	Permeance ($\times10^{-8}$mol·m^{-2}·s^{-1}·Pa^{-1})	H_2/N_2	H_2/CH_4	Ref.
ZIF-8	**α-Al_2O_3 tube**	**100**	**5.2**	**63.9**	**7.2**	**7.1**	**This work**
ZIF-8	**α-Al_2O_3 tube**	**100**	**14.3**	**20.8**	**10.3**	**10.4**	**This work**
SIM-1	α-Al_2O_3 tube	200	32.97	8.5	2.6		[1]
ZIF-8	Polymer tube	100	80	197	4.3	--	[2]
ZIF-8	α-Al_2O_3 tube	200	2.1	99	3.2	3.96	[3]
ZIF-8 [1]	α-Al_2O_3 tube	3000	25.3	5730	15.4	--	[4]
ZIF-8	YSZ tube [2]	100	1.88	154	11	13	[5]
ZIF-8	α-Al_2O_3 disc	--	--	17	5.7	--	[6]
ZIF-8	α-Al_2O_3 disc	--	3.8	23	9.6	10	[7]
ZIF-8	α-Al_2O_3 disc	--	2.5	10	--	16	[8]
ZIF-8	α-Al_2O_3 disc	200	3.8	40	~8.5	~9.6	[9]
ZIF-8	α-Al_2O_3 disc	--	2.2	17	11.6	13	[10]
ZIF-8	Titania disc	100	2.5	5.1	11.6	11.3	[11]
ZIF-8	α-Al_2O_3 disc	--	--	17	11.6	13.0	[12]

[1] In the membrane, the porous tube was functionalized with 3-aminopropyltriethoxysilane (APTES);

[2] YSZ* tube: hollow yttria-stabilized zirconia fiber support

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