In-situ growth of MOF nanofillers in Pebax matrix for excellent CO_2 permeability improvement

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Characterization

Surface and cross-sectional morphologies of membrane samples were taken in JEOL JSM-6510L scanning electron microscope after coated by platinum. The chemical structure of Pebax membranes and Pebax/ZIF MMMs was characterized by FTIR-ATR spectrometer (VERTEX 70, Germany) over a wavenumber range of 4000~400 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans per spectrum. X-ray diffraction (XRD) was performed using a PANalytical Empyrean instrument (Netherlands) to characterize the samples. Thermogravimetric analysis (TGA) was carried out using a TG 209 instrument (NETZSCH, Germany) to test the thermal stability of the Pebax/ZIF-8 MMMs. The thermal behavior of the membranes was investigated using differential scanning calorimetry (DSC 204 F1, NETZSCH, Germany) in a dual-scan mode. Tensile tests were performed using a universal material testing machine (INSTRON 5900 Series, Instron Corporation, USA) to evaluate the mechanical properties of the membranes. The specimens were prepared with dimensions of 5 cm × 1 cm (length × width), and the gauge length was set at 3 cm. The crosshead speed was maintained at 100 mm/s, and three replicate samples were tested for each membrane composition to ensure statistical reliability.

Gas permeation test

Gas permeation measurements were conducted on a home-made constant-volume apparatus using the time-lag method. Gases were tested in the sequence of N_2 and CO_2 under 35 °C and 3.5 atm. The gas permeability could be calculated by the following Equation 1:

$$P = \frac{273 \times 10^{10}}{760} \frac{Vl}{AT\left(p_2 \times \frac{76}{14.7}\right)} \frac{d_p}{d_t} \quad (1)$$

Where dp/dt is the steady increase rate of downstream-pressure, V is the volume of the downstream chamber (cm^3), l is the membrane thickness (cm). A is the effective test area of the membrane (cm^2), T is the operating temperature (K) and p_2 is the upstream operating pressure (psi). Each sample was independently measured for three times and the average value was taken.

The gas permeation theory[1]: The pure gas permeability (P) with the unit of Barrer (1 Barrer=10^{-10} cm^3(STP) cm/ (cm^2 s cm Hg) can be expressed by Fick's Law as the following Equation 2:

$$P = D \times S \quad (2)$$

Where D (cm^2/s) is the diffusion coefficient (diffusivity), S (cm^3 (STP) /cm^3 cm Hg) represents the sorption coefficient (solubility). The ideal selectivity of gas A over gas B ($\alpha_{a/b}$) is defined as the ratio of their permeabilities as Equation 3 shows:

$$\alpha_{\frac{A}{B}} = \frac{P_A}{P_B} = \left[\frac{D_A}{D_B}\right] \times \left[\frac{S_A}{S_B}\right] \quad (3)$$

Using the diffusion time lag (θ) extrapolated from the plot of pressure with time (**Figure S2**) at steady state to the time axis, the diffusivity can be calculated by Equation 4:

$$D = \frac{l^2}{6\theta} \quad (4)$$

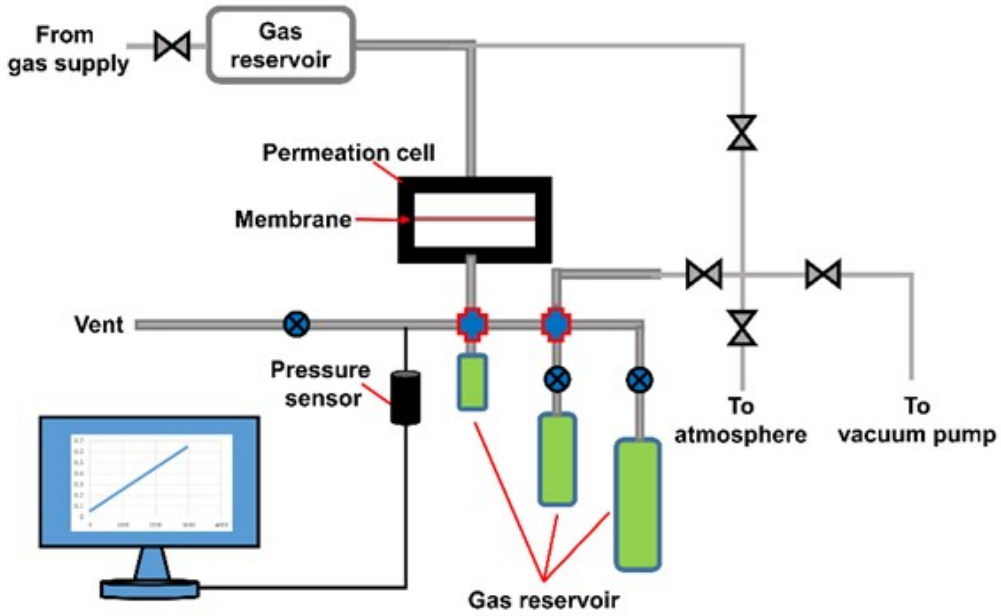

Figure S1 The illustration of the home-made apparatus for gas permeation test

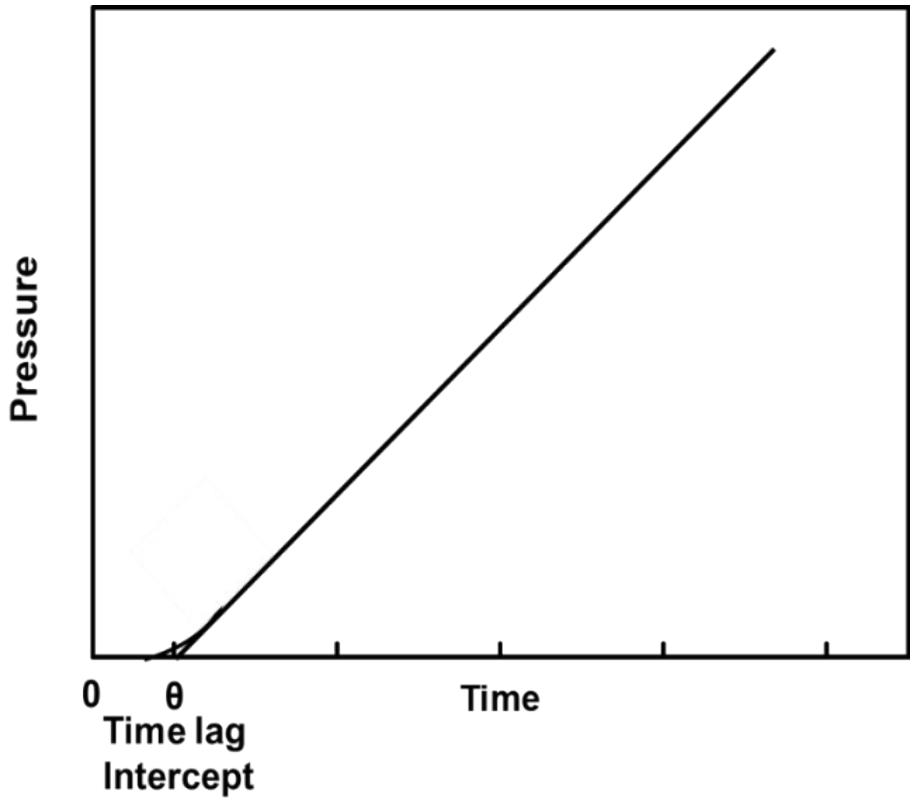

Figure S2 Time-lag derived from the gas permeation curves

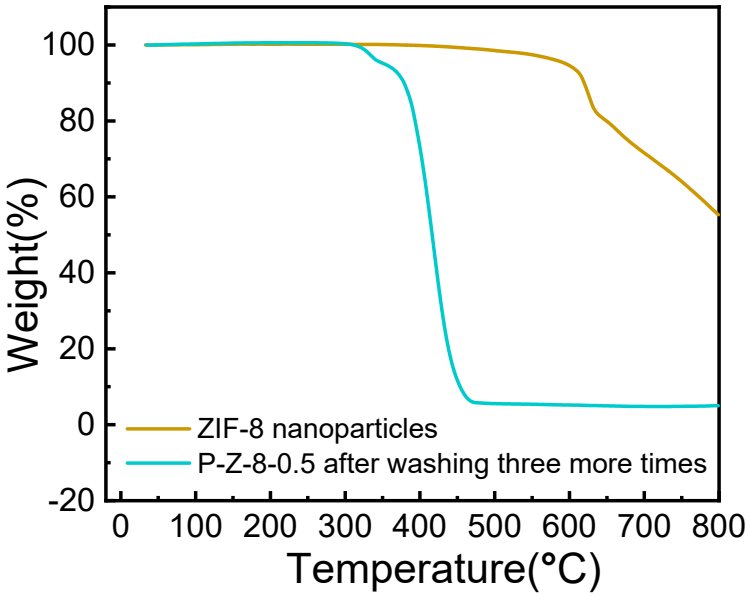

Figure S3 TGA curves of pure ZIF-8 nanoparticles and the P-Z-8-0.5 MMM after washing three more times

The cross-sectional SEM images was shown in Figure S4. The results indicated that the thickness of the fabricated membranes are comparable, with negligible variations among different samples.

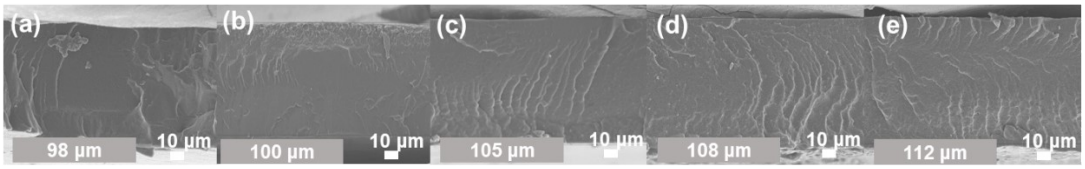

Figure S4 (a-e) The cross-sectional SEM images of P-Z-8-0, P-Z-8-0.2, P-Z-8-0.5, P-Z-8-0.8and P-Z-8-1.0, respectively

As clearly illustrated in Figure S5, the Zn, C, N, and O elements are homogeneously distributed throughout the membrane matrix. This uniform elemental distribution provided compelling evidence that ZIF-8 has been successfully synthesized and dispersed uniformly within the Pebax matrix.

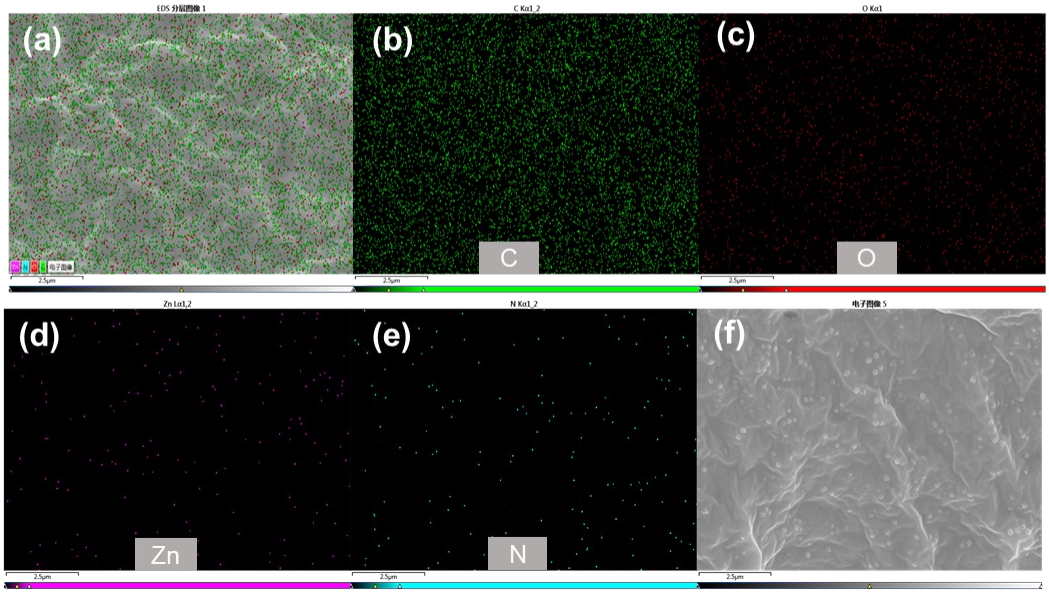

Figure S5 EDS elemental mapping image of P-Z-8-0.5 membrane

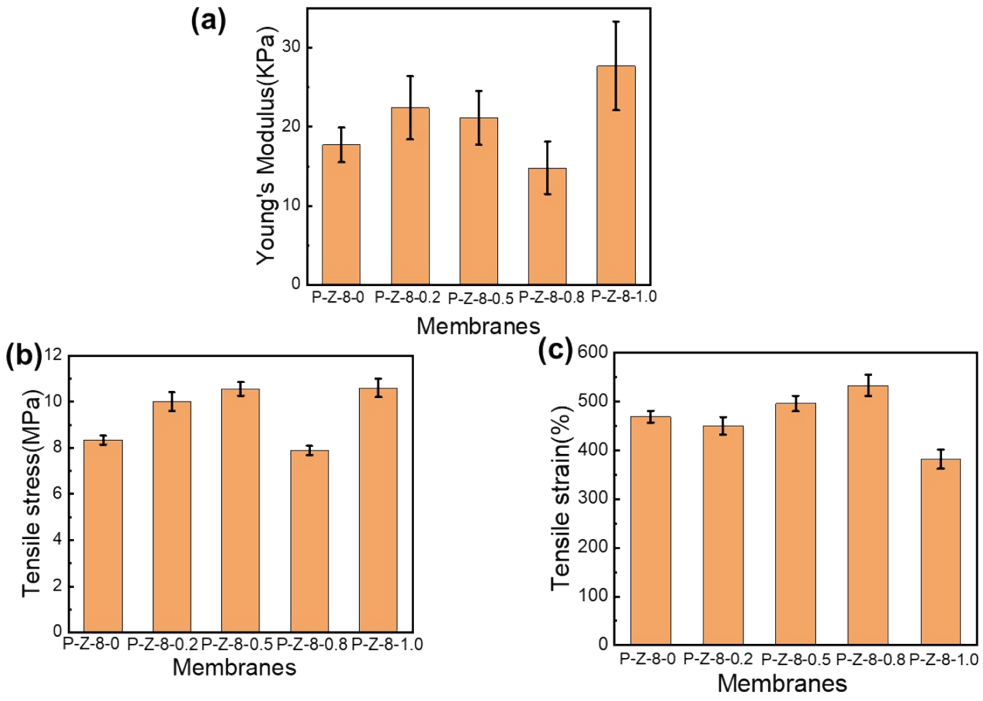

Figure S6 (a) Young's modulus, (b) tensile strength and (c) elongation at break of P-Z-8 MMMs

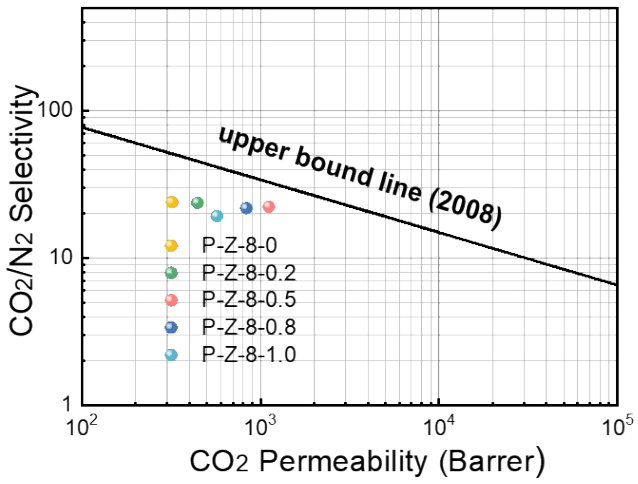

Figure S7 CO_2 permeability and CO_2/N_2 selectivity of the MMMs. The black line represented the 2008 Robeson upper bound

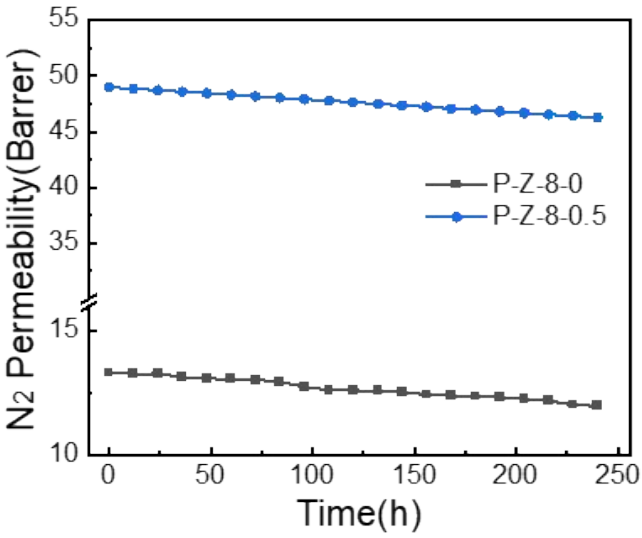

Figure S8 N_2 permeability variation during 10 days for P-Z-8-0 and P-Z-8-0.5

Table S1 Mean ± SD deviation of permeability/selectivity values for replicate membranes

	N_2 Permeability (Barrer)	CO_2 Permeability (Barrer)	CO_2/N_2
P-Z-8-0	13.3±2.7	319±20	23.9±1.5
P-Z-8-0.2	18.6±1.6	443±18	23.7±1.3
P-Z-8-0.5	49.9±1.8	1116±32	22.3±1.2
P-Z-8-0.8	38.2±2.4	833±29	21.8±0.7
P-Z-8-1.0	29.5±3.2	569±25	19.3±0.8

Table S2 Mean ± SD deviation of permeability/selectivity values for replicate membrane

	Young's Modulus (KPa)	Tensile stress (MPa)	Tensile strain (%)
P-Z-8-0	17.7±2.2	8.3±0.2	469.1±12
P-Z-8-0.2	22.4±4.0	10.1±0.4	450.3±18
P-Z-8-0.5	21.1±3.4	10.5±0.3	496.8±16
P-Z-8-0.8	14.8±3.3	7.9±0.2	533.2±22
P-Z-8-1.0	27.7±5.6	10.6±0.4	382.5±20

Reference

[S1] S.W. Rutherford, D.D. Do, Review of time lag permeation technique as a method for characterisation of porous media and membranes, Adsorption, 3 (1997) 283-312.