Electronic Supporting Information

Mixed-matrix membranes containing functionalized porous metal-organic nanoballs for effective separation of CO_2 /CH_4 mixture

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1 Experimental Procedures

1.1 Synthesis of MOP-SO_3Na

The sulfonic group functionalized nanoballs were synthesized according to the previously reported procedure[S1]. NaH_2(5-SO_3-1,3-BDC) (269.0 mg) in MeOH (8.0 mL) was mixed with a MeOH/DMA solution (15.0 mL, v:v = 1:1) of $Cu_2(OAc)_4 \cdot H_2O$ (200 mg) in a glass vial (50.0 mL) and stirred for 10 min at room temperature. Then, 5.0 mL of DMA was added into this solution and the vial was open and stood at room temperature. Homogeneous dark-blue block crystals were collected after 10 days and washed carefully with ethanol and DMA.

1.2 Synthesis of MOP-OH

H_2(5-OH-1,3-BDC)(365 mg) in MeOH (10.0 mL) was mixed with a MeOH (30.0 mL) solution of $Cu_2(OAc)_4 \cdot H_2O$ (400 mg) and stirred. Then, 10.0 mL DMA was added into this solution and the mixed solution was kept for 20 days at room temperature. At last the crystals were collected and washed with DMA and a little acetone.

1.3 Preparation of mixed-matrix membranes

Polysulfone (PSF) (kindly supplied by BASF) was degassed at 423 K overnight under vacuum to remove the adsorbed water. To prepare the MMMs, the required amount of MOP to achieve a given weight loading was dispersed in 5.0 mL of 1-methyl-2-pyrrolidinone. Then polymer were added to this suspension for several times, leading to a viscous solution. For comparison purposes, a membrane based on the neat polymer was prepared following an identical procedure, but without MOP incorporation. To prepare membranes, the homogeneous suspension was poured on a glass surface, we use casting machine to prepare membranes. To remove the solvent in the membranes, the glass was placed in a vacuum oven at 323 K for 2 days.

2 Characterization techniques and results

2.1 X-ray diffraction

X-ray diffraction analysis of the membranes were carried out on a SHIMADZU XRD-6000-X-ray diffractometer in reflection mode using Cu Ka radiation (λ = 1.5406 Å), The 2θ range from 3° to 55° was scanned with a step size of 0.05°.

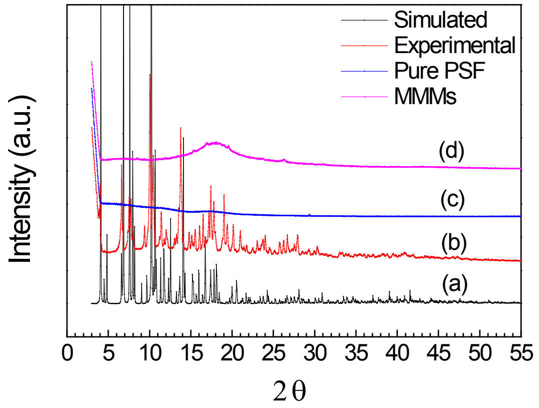


Fig. S1 X-ray diffractions of (a) simulated MOP-SO_3Na, (b) experimental MOP-SO_3Na, (c) PSF membrane, and (d) MOP-SO_3Na/PSF MMMs.

2.2 FTIR analysis

The FTIR analysis was performed on Nicolet 6700 FTIR spectrophotometer. Spectra were recorded in the 4000-500 cm^{-1} wavenumber range.

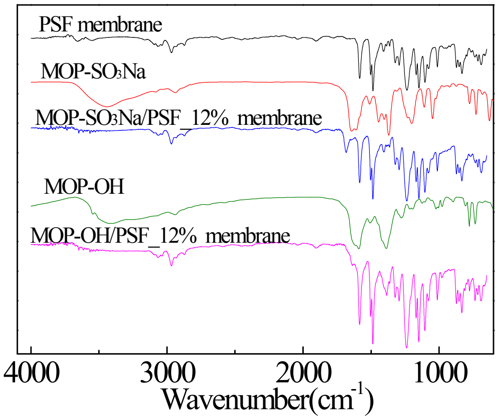


Fig. S2 FTIR spectra of PSF membrane, MOP-SO_3Na, MOP-SO_3Na/PSF_12% membrane, MOP-OH, MOP-OH/PSF_12% membrane.

2.3 TGA analysis

The TGA analyses were performed at a heating rate of 10 ℃/min under nitrogen on a TGA 1/1100 SF instrument.

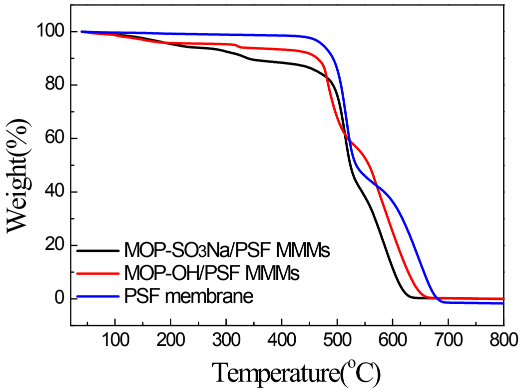


Fig. S3 TGA plots of PSF membrane, MOP-SO_3Na/PSF_12% membrane, MOP-OH/PSF_12% membrane.

2.4 XPS analysis

X-ray photoelectron spectroscopy data were obtained using an ESCALAB 250 electron spectrometer (Thermo Fisher Scientific company, US) .

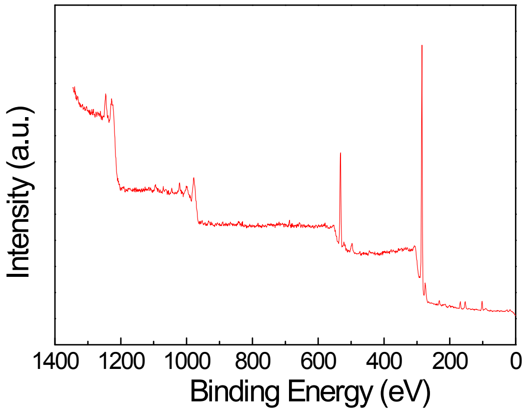


Fig. S4 XPS plots of MOP-SO_3Na/PSF_12% membrane surface.

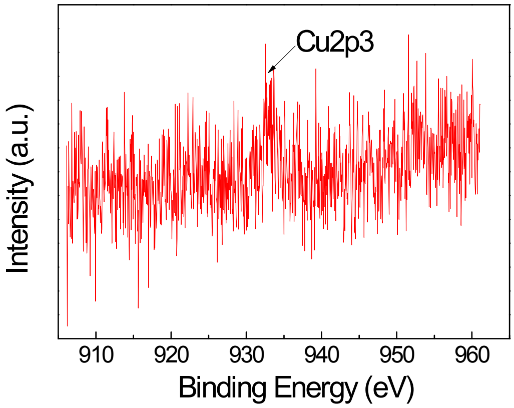


Fig. S5 The enlarged XPS for Cu2p3 site.

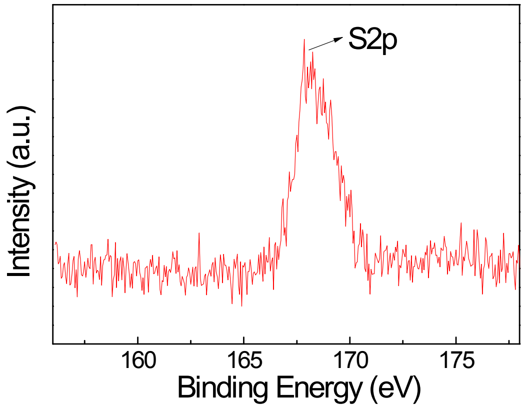


Fig. S6 The enlarged XPS for S2p site.

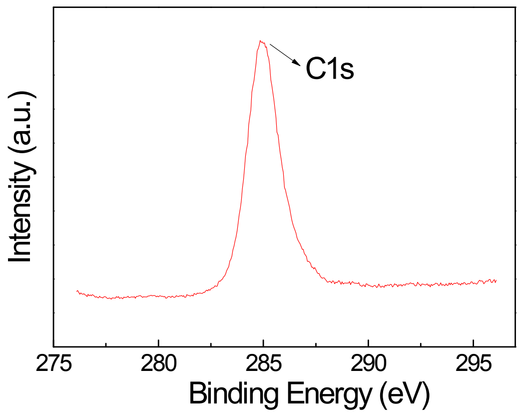


Fig. S7 The enlarged XPS for C1 site.

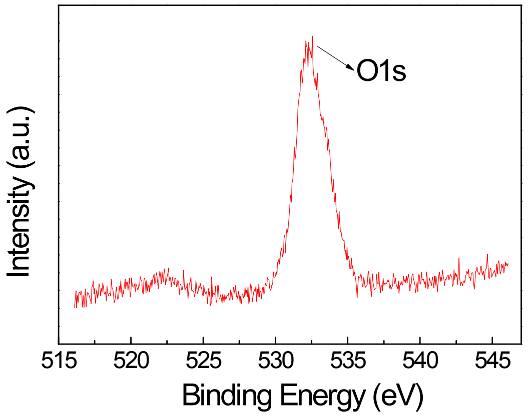


Fig. S8 The enlarged XPS for O1 site.

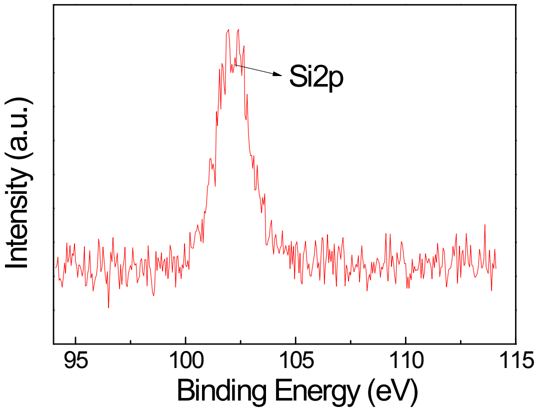


Fig. S9 The enlarged XPS for Si2p site.

2.5 Gas adsorption and desorption analysis

The experimental gas adsorption and desorption isothermals of CO_2, CH_4 were measured at 298 K using gas adsorption equipment.

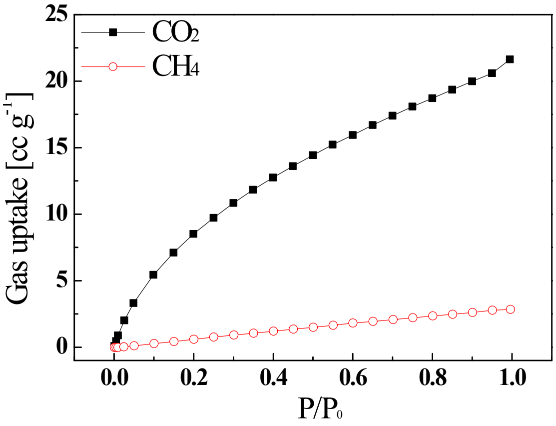


Fig. S10 Experimental adsorption and desorption isotherms of CO_2 and CH_4 in MOP-SO_3Na at 298 K .

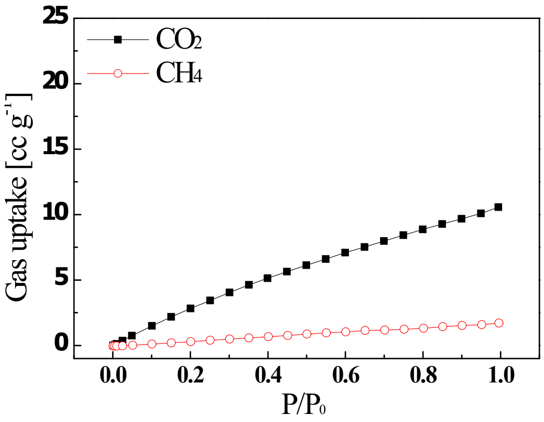
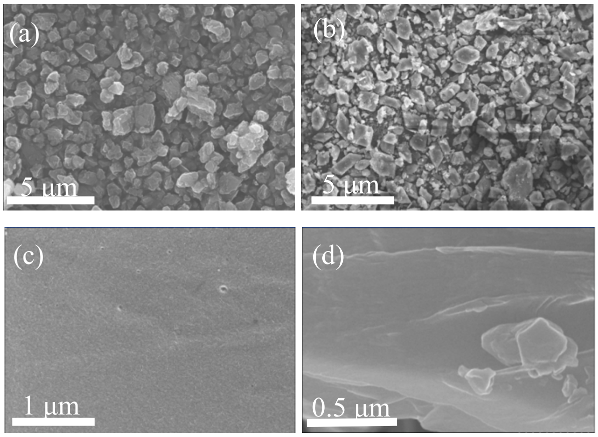


Fig. S11 Experimental adsorption and desorption isotherms of CO_2 and CH_4 in MOP-OH at 298 K.

2.6 SEM and EDS analysis

The membrane morphologies were observed via a scanning electron micrographs. (FEI, a XL-30 ESEM-FEG microscope). The gold-coated specimens were operated under 10-20 KV acceleration voltage.



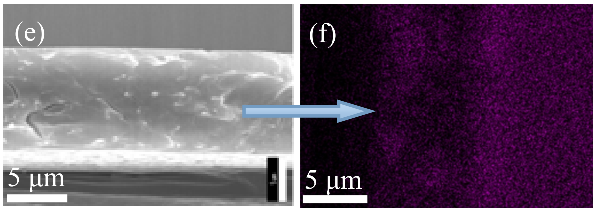


Fig. S12 SEM micrographs of (a) MOP-SO_3Na nanocrystals, (b) MOP-OH nanocrystals, (c) surface of MOP/PSF_12 wt% membrane, (d,e) cross-section of MOP/PSF_12 wt% membrane; (f) EDXS mapping of MOP/PSF_12 wt% membrane (Cu signal: purple).

2.6 Membrane thickness measurement

Membrane thickness was determined using a digital micrometer with an accuracy of 1 µm. The measurement was performed at least at several different locations within each membrane and then averaged. In this work, the membranes' thickness we made using the casting machine is about 15 µm.

2.7 Gas permeation experiments

Gas permeability experiments were evaluated for CO_2 and CH_4 using a custom-built gas flux measuring apparatus (Fig. S3) . The apparatus consists of a permeation module. This module exposes a membrane area of 3.14 cm^2 to the gas. We placed the membranes in the permeation module. Then an equimolar mixture of CO_2 and CH_4 was employed as feed. Helium was used as sweep gas for the permeate stream. Finally, the gas chromatograph at the permeation side was used to detect the constitute of the mixture online. Each membrane was fabricated and measured at least 3 times to ensure the reproducibility of the results.

Gas separation performance is defined by the separation factor (α) and the gas permeabilities (P) of the individual components [S11]. The permeability for the i-component (Pi) was calculated as follows:

$$P_i = \frac{\Phi_{n,i} \cdot \delta}{\Delta \mathrm{P_i} \cdot A} \tag{1}$$

Where $\Phi_{n,i}$ denotes the molar flow rate of i-compound, δ is the thickness of the membrane, $\triangle P_i$ is the partial pressure difference of the i-component across the membrane and A is the membrane area. The SI unit for the permeability is mol s^{-1} m^{-1} Pa^{-1}. However, here gas permeabilities are reported in the widely used non-SI unit Barrer, where 1 Barrer = 3.35 × 10^{-6} mol m^{-1} Pa^{-1} s^{-1}.

$$\mathrm{P(barrer)} = 10^{-10} \frac{\mathrm{cm^3(STP) \cdot cm}}{\mathrm{cm^2 \cdot s \cdot cmHg}} \tag{2}$$

The separation factor of mixed gas selectivity (α) was calculated as the ratio of the permeability of the more permeable compound (CO_2) to the permeability of the less permeable compound (CH_4).

$$\alpha = \frac{P_{CO_2}}{P_{CH_4}} \tag{3}$$

Fig. S13 The gas flux measuring apparatus.

2.7 Transient permeation curve

The gas separation performance was conducted before a period evacuation. When the system reaches a steady state, the data recording starts.

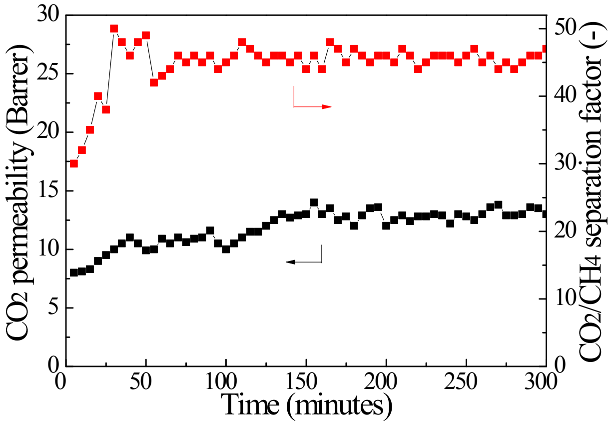


Fig. S14 Evolution of the CO_2 permeability (left-axis) and the CO_2/CH_4 separation factor (right-axis) of MOP-SO_3Na/PSF_12% membrane (thickness of about 15 μm). Operation conditions: gas feedstock mixture of CO_2:CH_4 = 1:1, T = 298 K, ΔP = 3 bar.

3 Comparison of gas permeability and selectivity of MMMs

Table S1 Comparison of gas permeability and selectivity of MMMs

Filler	Loading (wt %)	Operation conditions			$P(CO_2)$ [Barrer]	S (CO_2/CH_4)	Ref.
		Analysis	T (K)	ΔP (atm)			
MCM-41	10	single gas			10.50	17.92	S2
	20				11.40	18.91	
	30				20.50	19.52	
SWNT	5	single gas	308	4	5.12	18.82	S3
	10				5.19	18.41	
	15				4.52	16.09	
HKUST-1	5	single gas			7.70	21.50	S4

SiO$_2$	5	single gas	308	4.4	7.70	24.84	S5
	10				9.30	23.25	
	15				12.90	19.25	
	20				19.70	17.59	
MCM-48	10	single gas	308	4	8.45	25.47	S6
	20				18.21	23.58	
MIL-68(Al)	4	mixture (1:1)	308	2.75	4.70	32.20	S7
	8				5.30	31.70	
SNW-1	12	mixture (1:1)	298	3.5	22.40	35.00	S8
	12	single gas	298	3.5	25.04	27.00	
ZIF-8	16	mixture (1:1)	308	2	12.10	39.80	S9
NH$_2$-MIL-53(Al)	8	mixture (1:1)	308	1	4.90	29.70	S10
	16				5.70	34.00	
	25				6.20	46.00	
	40				10.60	17.00	
	25		263	10	2.40	117.00	
Porous polyhedrons	8	mixture (1:1)	298	3	9.5	36.71	This work
	12				12.94	45.68	
	18				15.18	34.33	

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