UK-China Bilateral Workshop MEEA 2018

Imperial College London

Barrer Centre

Preparation and Application of Ceramic-supported Metal-Organic Framework Membranes

<u>Kang Huang</u>

Prof. Kang Li, Post-doctor supervisor

Barrer Centre, Department of Chemical Engineering, Imperial College London, UK

Prof. Wanqin Jin, PhD supervisor

State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, China

15 October, 2018
Nanjing, China

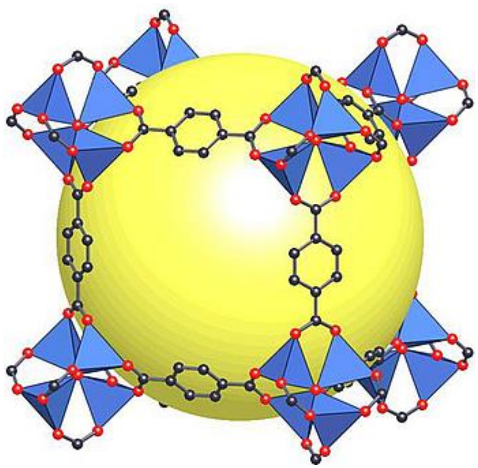
Outline

- Background (MOFs and MOF membranes)
- Introduction (my works about MOF membranes)
- Main
  - Inner MOF membranes by circulation convection method
  - Micropatterned UiO-66 membranes
- Conclusion

Background

❖ Metal-organic frameworks (MOFs)

Metal–organic frameworks (MOFs) are hybrid **inorganic–organic** materials consisting of **metal ions** or **clusters** coordinated to **organic ligands** to form one-, two-, or three-dimensional structures.



- High surface areas
- Tailor-made pores
- Designable structures
- Preferential adsorption

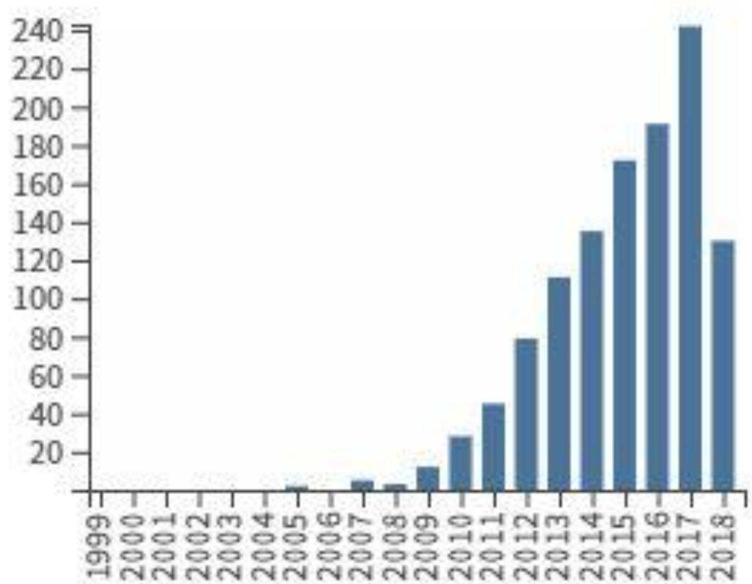
Ref.

O. M. Yaghi, Nature, 1999, 402, 276-279; G. Férey et al., Science, 2005, 309, 2040;
Q. Li et al., Science, 2009, 325, 855; R. Banerjee et al., J. Am. Chem. Soc., 2009, 131, 3875.
Y. Liu, Y. Ban, W. Yang, Adv. Mater. 2017, 29, 1606949.

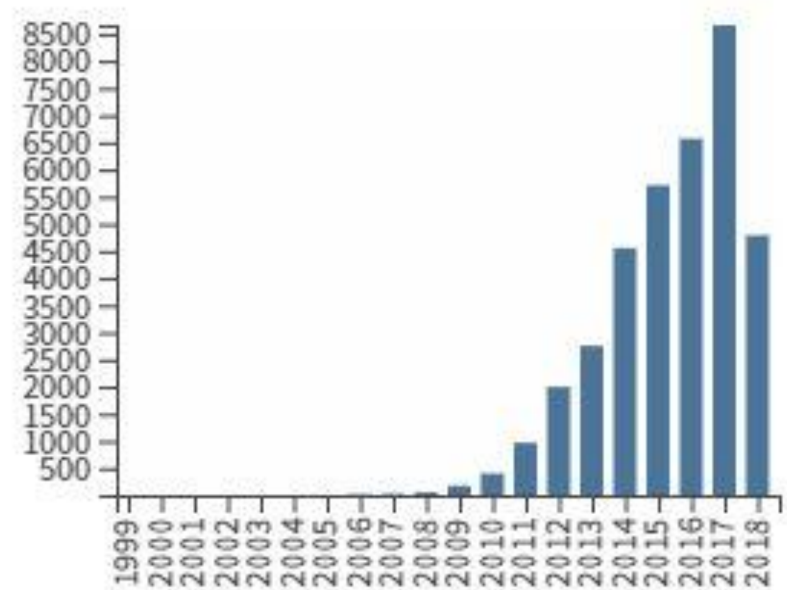
Background

❖ Prospection

- Excellent candidates for applications in membrane separation fields.
- Publications and Citations (**pure MOF membranes**)



Total Publications by Year

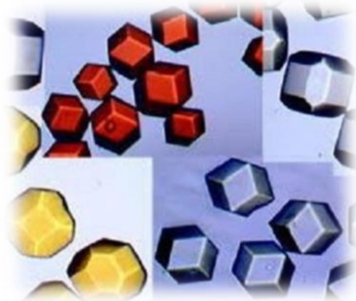


Sum of Times Cited by Year

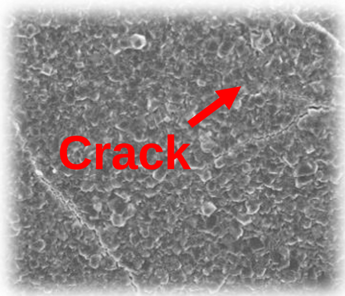
TOPIC: (metal-organic framework or ZIF) AND (membrane) AND (separation)
Data: Web of science

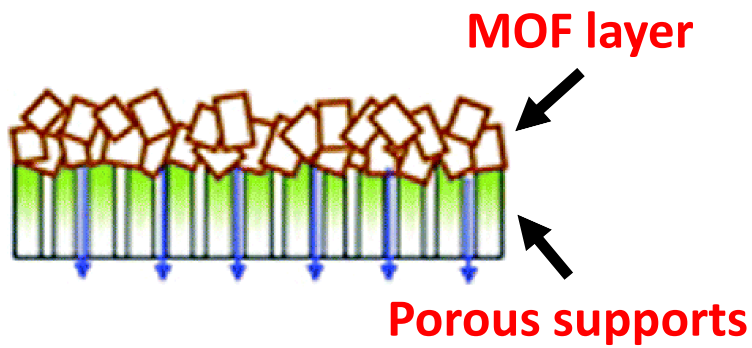
Introduction

What can we do?



MOF crystal examples





- high flux and high selectivity

◆ Ceramic supports

✓ Mechanical strength (over 10 N)

✓ Chemical stability (acid & alkali)

✓ Thermal stability (over 1000 ℃)

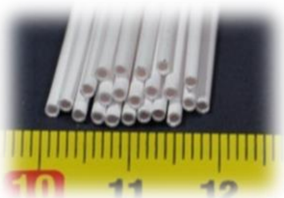
Introduction

What I have done:

CERAMIC SUPPORTS

Disc

Tube (e.g., Hollow Fibre)



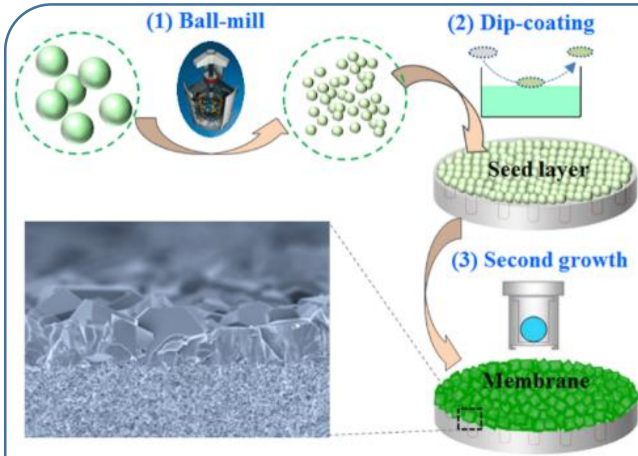
Introduction

What I have done:

CERAMIC SUPPORTS

Disc: flat, smooth…

①



Novelty:

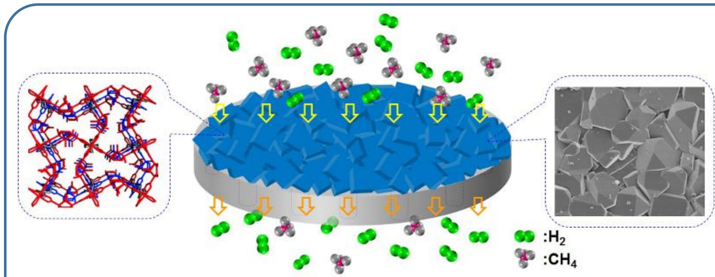
High-energy Ball-milling Method for Seeding

Application:

Enantioseparation (2-methyl-2,4-pentanediol)

Chiral MOF Membrane for Enantioseparation of Racemic Diols

②



Target:

Verification of reactive seeding method for metal-carboxylate MOF

Application:

H2 recovery

[Zn2(cam)2dabco] (Zn-CD) membrane on porous ZnO support

Introduction

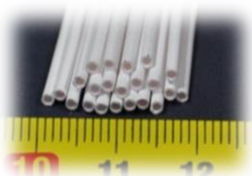
What I have done:

CERAMIC SUPPORTS

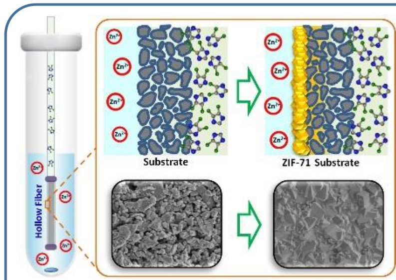
Disc:

- Fabrication of homochiral MOF membrane for enantioseparation of racemic diols
  K Huang, WQ Jin, et al., *Sep. Purif. Technol.,* 2013, 119, 94.
- Preparation of novel metal-carboxylate system MOF membrane for gas separation
  K Huang, WQ Jin, et al., AIChE Journal 2013, 59, 4364.

Hollow Fibre: Higher membrane area to volume ratio



①

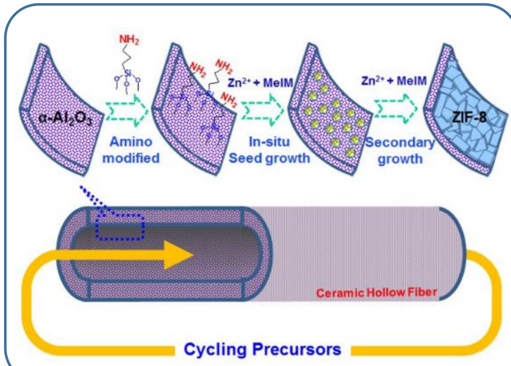


Novelty:
Hydrophobic MOF membranes on hollow fiber

Application:
Recovery of ethanol from ethanol/water mixture

Hydrophobic ZIF-71 Membrane Fabricated by Contra-Diffusion

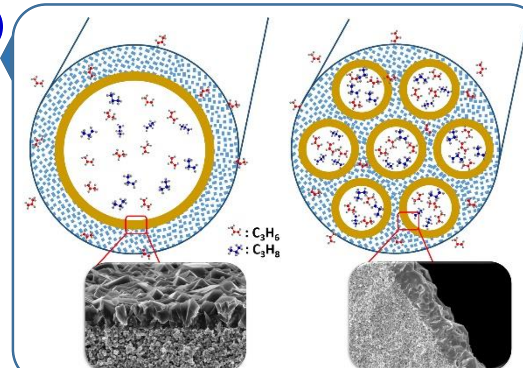
②



Novelty:
Inner MOF membranes

Application:
H_2 recovery
Propylene/propane

③



Introduction

What I have done:

CERAMIC SUPPORTS

Disc:

- Fabrication of homochiral MOF membrane for enantioseparation of racemic diols

  K Huang, WQ Jin, et al., *Sep. Purif. Technol.,* 2013, 119, 94.
- Preparation of novel metal-carboxylate system MOF membrane for gas separation

  K Huang, WQ Jin, et al., *AIChE J.* 2013, 59, 4364.

Hollow Fibre:

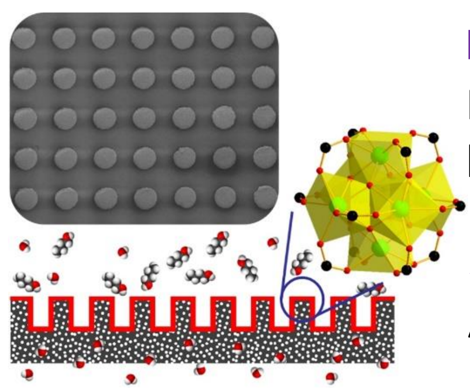
- Hydrophobic ZIF-71 Membrane Fabricated by Contra-Diffusion

  K Huang, WQ Jin, et al., *ACS Appl. Mater. Inter.,* 2015, 7, 16157.
- ZIF-8 membrane on the inner-surface of ceramic hollow fiber via cycling precursors

  K Huang, WQ Jin, et al., *Chem Commun*., 2013, 49, 10326
- High C_3H_6 Selective MOF Membranes in Confined Spaces via Convective Circulation

  K Huang, K Li, et al., *Adv. Mater. Interfaces*, 2018, 1800287

Designed Special Configuration:



Micropatterned MOF Membranes

Novelty:

Miniaturization of MOF membranes by patterning the membrane surface

Application:

A lab-on-a-chip device

Introduction

What I have done:

CERAMIC SUPPORTS

Disc:

- Fabrication of homochiral MOF membrane for enantioseparation of racemic diols
  K Huang, **WQ Jin**, et al., *Sep. Purif. Technol.,* 2013, 119, 94.
- Preparation of novel metal-carboxylate system MOF membrane for gas separation
  K Huang, **WQ Jin**, et al., *AIChE J.* 2013, 59, 4364.

Hollow Fibre:

- Hydrophobic ZIF-71 membrane fabricated by contra-diffusion
  K Huang, **WQ Jin**, et al., *ACS Appl. Mater. Inter.,* 2015, 7, 16157.
- ZIF-8 membrane on the inner-surface of ceramic hollow fiber via cycling precursors
  K Huang, **WQ Jin**, et al., *Chem Commun*., 2013, 49, 10326
- High C_3H_6 selective MOF membranes in confined spaces via convective circulation
  K Huang, **K Li**, et al., *Adv. Mater. Interfaces*, 2018, 1800287

Designed Special Configuration:

- Micropatterned MOF membranes with enhanced molecular sieving property
  K Huang, **K Li**, et al., *Angew. Chem. Int. Ed.*, 2018, DOI: 10.1002/anie.201809872

Inner MOF membranes

Motivation ?

(Prepare MOF membranes on disc substrates or exterior surface of tubes)

➡ MOF membranes are easily damaged during preparation, storage and module assembly.

Available way:

Prepare MOF membranes on the inner surface of tubular supports (e.g., hollow fiber)

Current method: (How to offer enough reactants for growth of MOF membranes)

- Interfacial microfluidic processing driven by syringe pump *Science 345, 72 (2014)*
- Cycling precursor driven by peristaltic pump *Chem. Commun., 2013, 49, 10326*

Disadvantages:

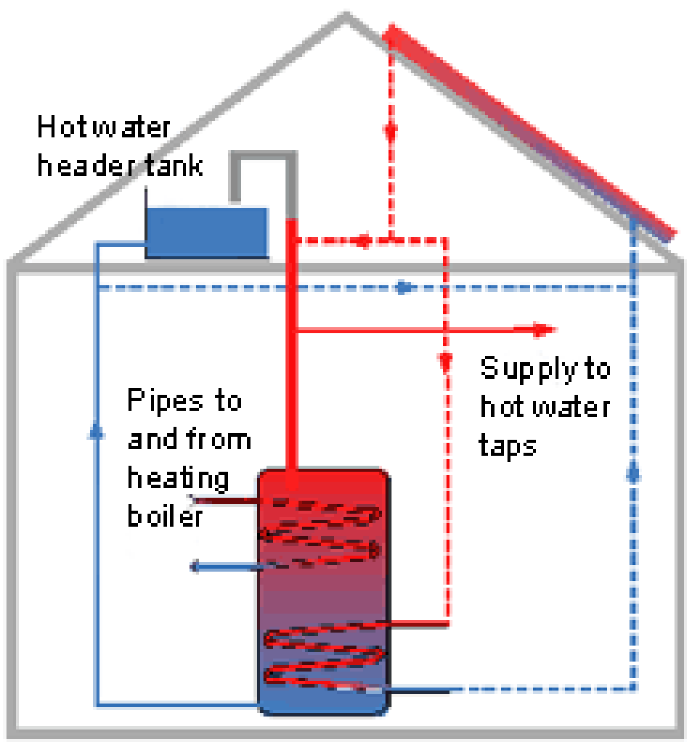
- Pulsed flow (peristaltic pumps)
- Volume limit (syringe pumps)
- Corrosion to the sealing parts
- **Effect of high temperature**

⇨

Alternative approaches are significant for the development of MOF membranes.

Research Plan

- **Domestic heating systems**



Pump-free Gravity Hot Water systems

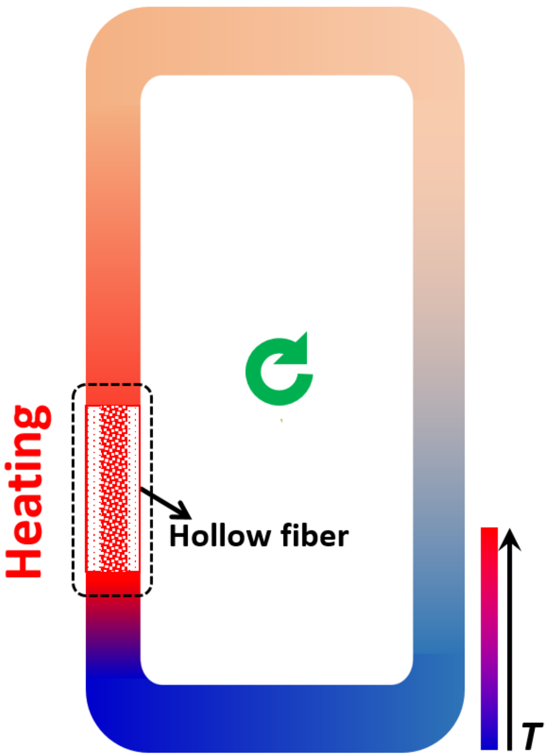
Hot water around the house by using only convective action.

Pump-free MOF synthesis system.

Convective circulation method

Research Plan

- Convective circulation

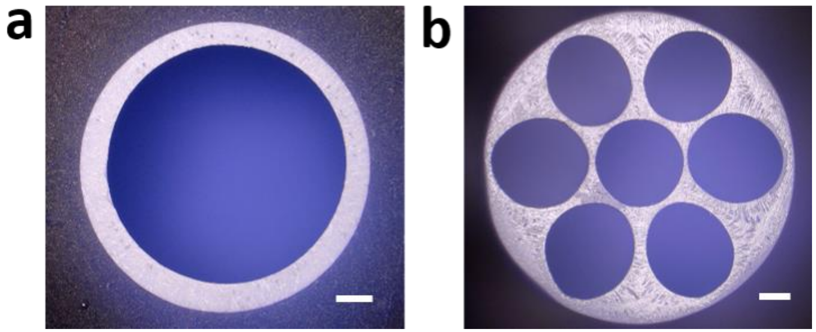


Schematic of convective circulation synthesis loop
Warm colours (Red): higher temperatures
Cold colours (Blue): lower temperatures

Convective circulation synthesising setup was built using stainless steel tubings

Research Results

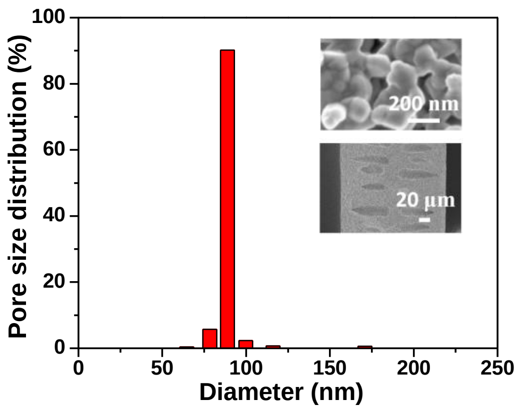
- Substrates: YSZ hollow fiber

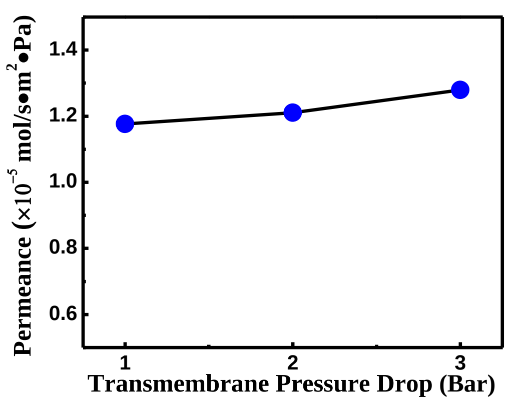


Scale bar: 250 μm

(a) YSZ hollow fibre and

(b) 7-bore micro-monolith substrates.



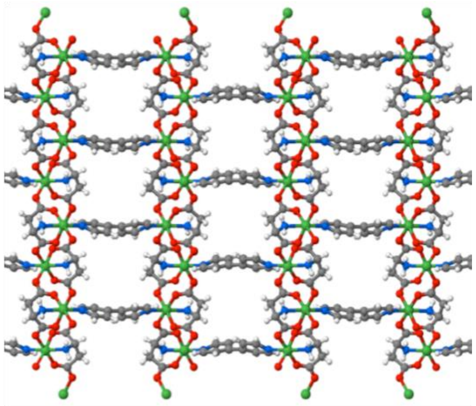


- Enhance the membrane area to volume ratio in assembled modules;
- Reduce the capital and operational costs for separation plants.

The mean flow pore size is ~90 nm.
N_2 permeance is 1.17 × 10^{-5} mol·m^{-2}·s^{-1}·Pa^{-1} (295 K, 1 bar)

Preparation of inner MOF membrane

Ni-LAB



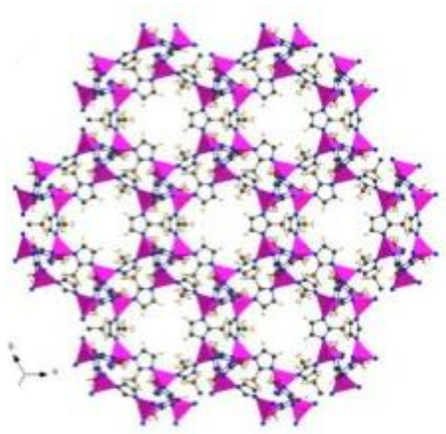
*Synthesis Temp.: **150 ℃***

[Ni_2(l-asp)$_2$(bipy)]

bipy: 4,4'-bipyridine
l-asp: L-aspartic acid

Ref.
Angew Chem Int Ed. 2006;118: 6645–6649.

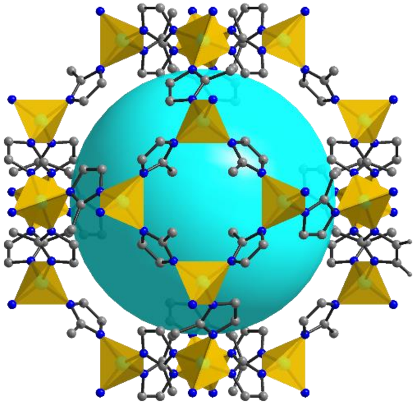
ZIF-67



*Synthesis Temp.: **25-120 ℃***

Ref.
J. Am. Chem. Soc. 137, 38, 12304-12311
Chem. Commun., 2016, 52, 12578-12581

ZIF-8

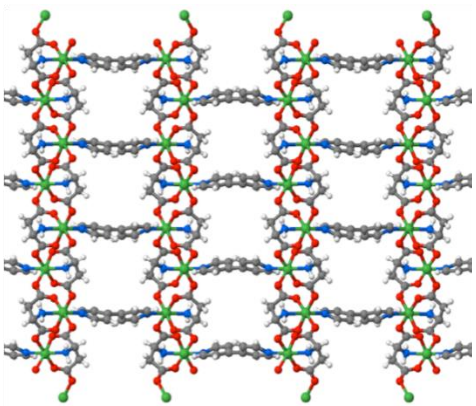


*Synthesis Temp.: **25-100 ℃***

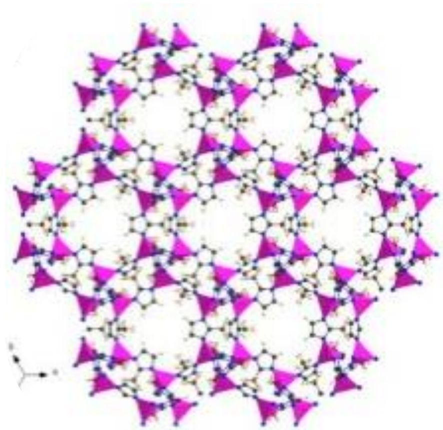
Ref.
J. Am. Chem. Soc. 2009, 131, 16000–16001
Chem. Commun., 2011, 47, 2071–2073

Preparation of inner MOF membrane

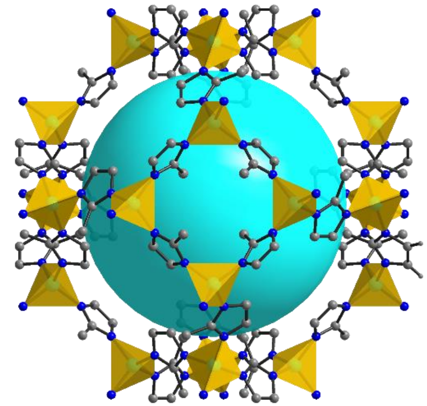
Ni-LAB

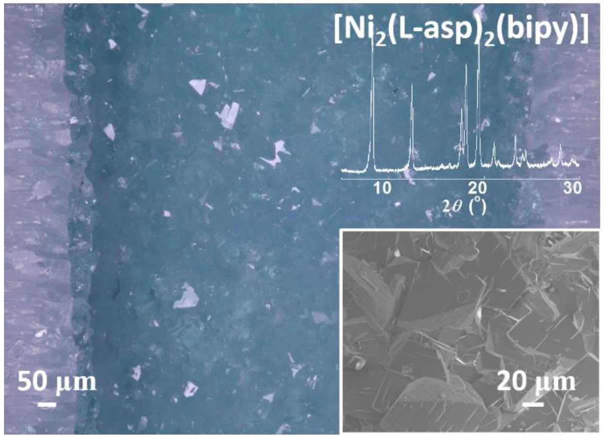


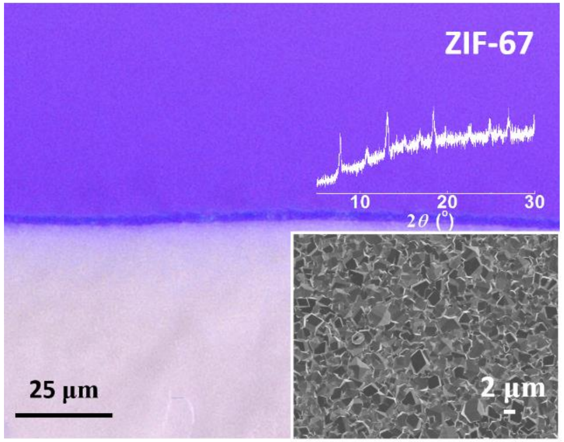
ZIF-67

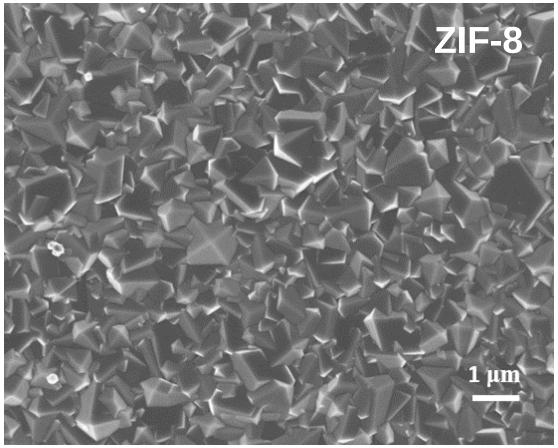


ZIF-8



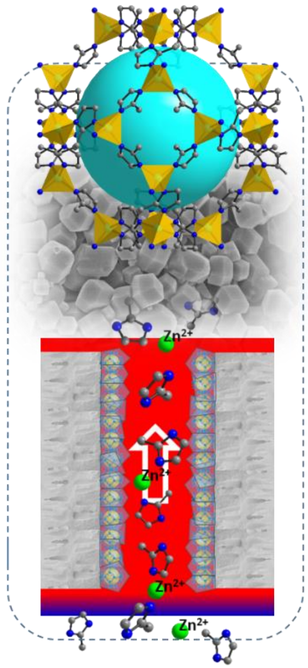






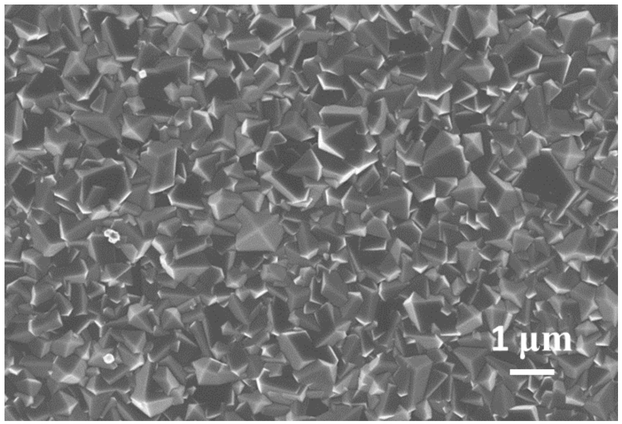
Support: YSZ ceramic substrates

ZIF-8 membrane characterizations

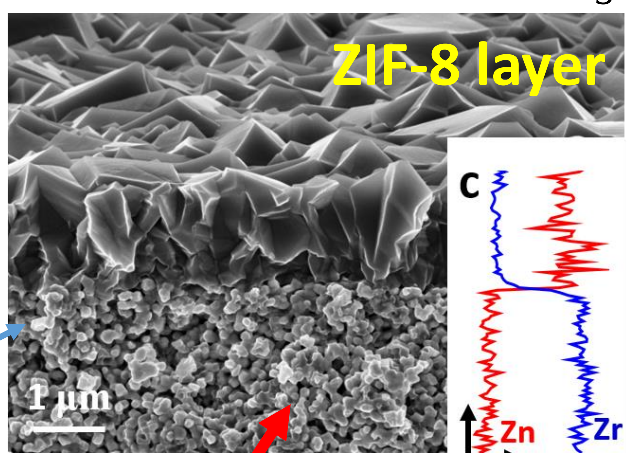


ZIF-8

Surface SEM image

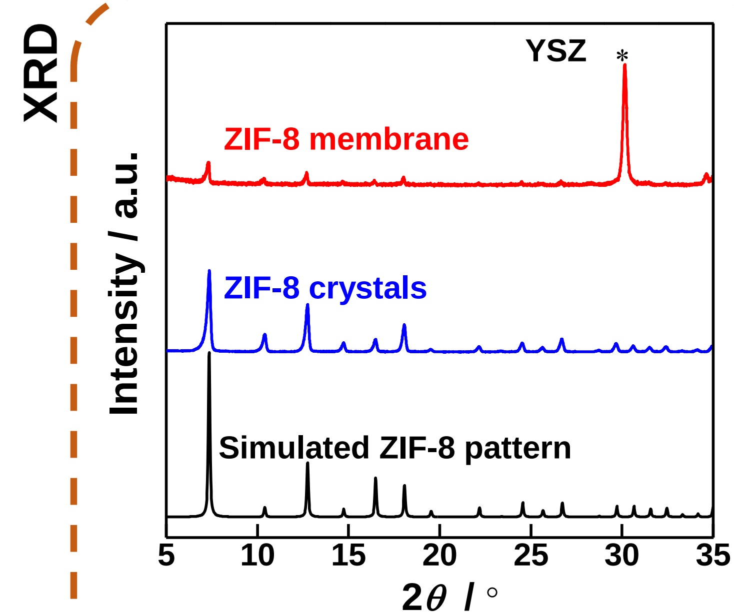


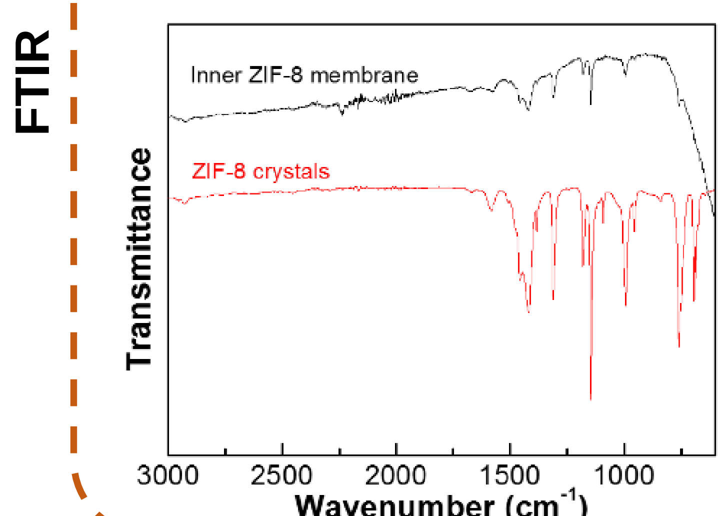
Cross-sectional SEM & EDX images



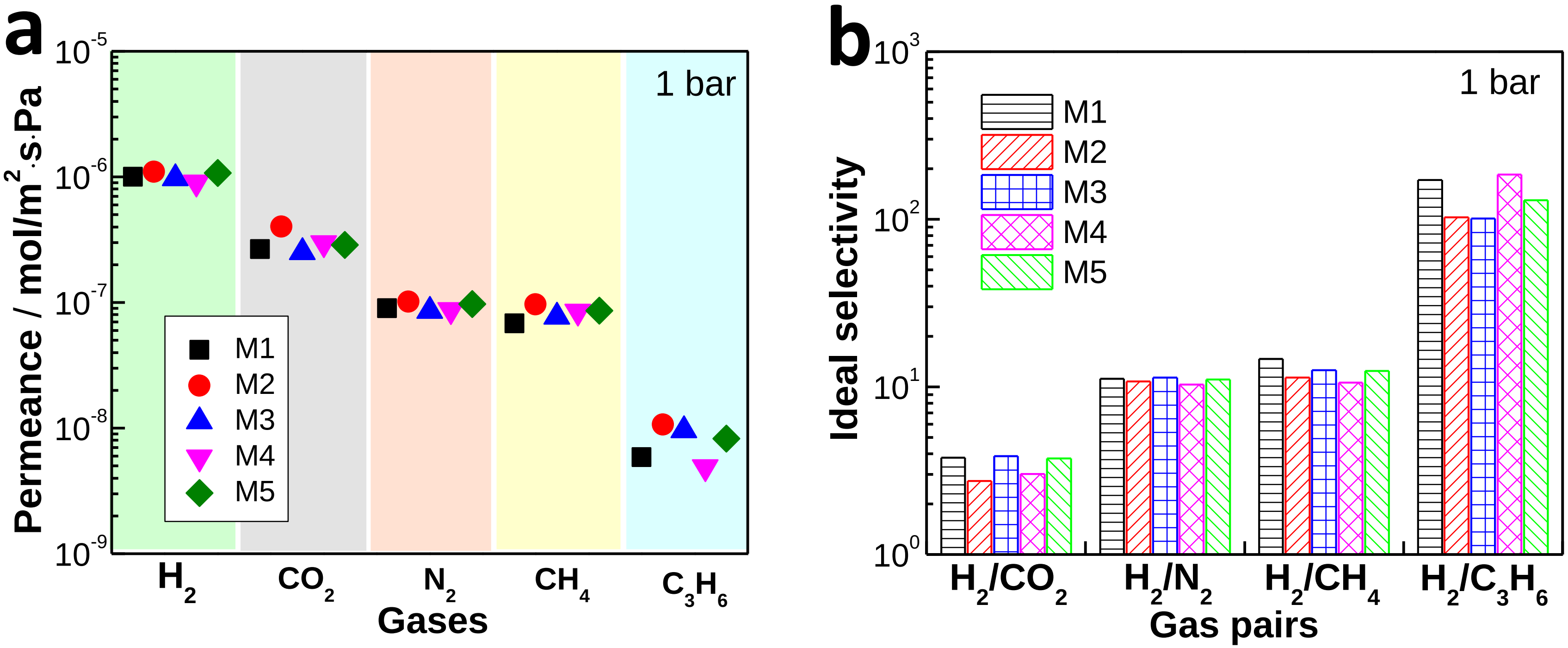
No obvious penetration

YSZ hollow fiber support





ZIF-8 membrane separation performance

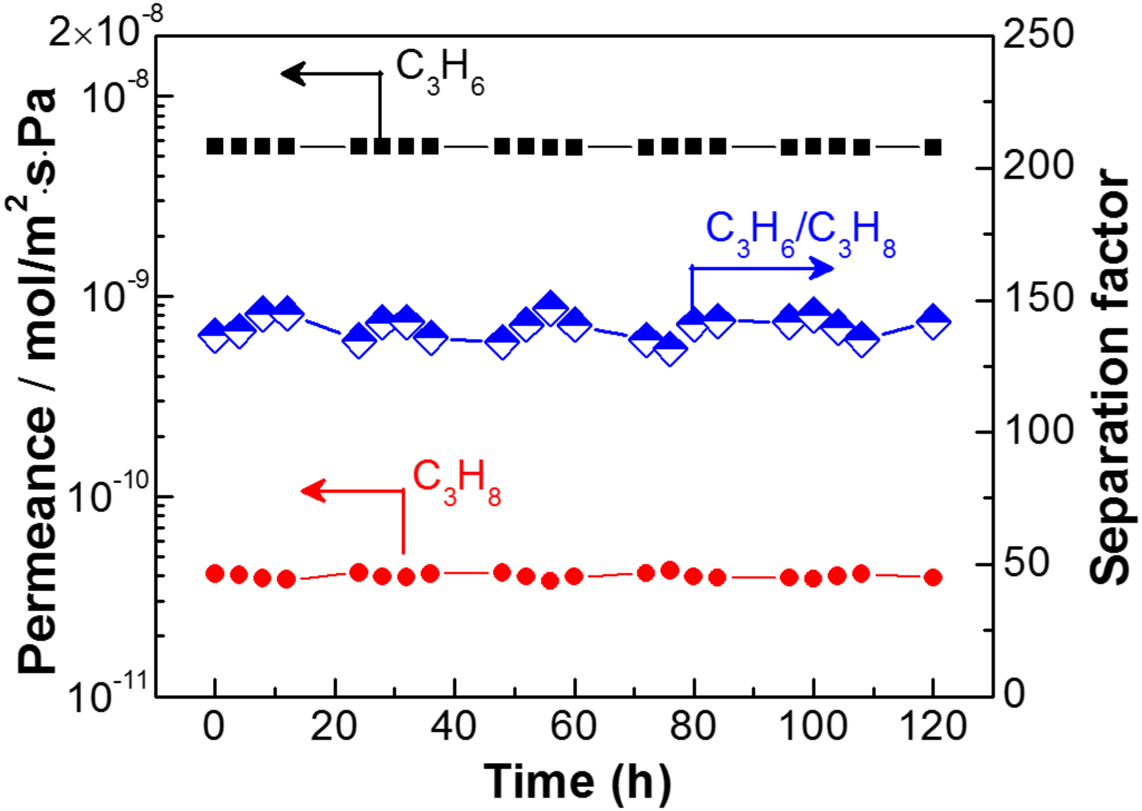


(a) Pure gas permeances and (b) ideal selectivities of H_2 over other gases for the five samples (M1-M5), confirming the consistency of membrane quality. The data were achieved through the constant-volume/variable-pressure setup

- Five ZIF-8 membranes were synthesized and showed very consistent performances when tested with five different gases.
- The gas permeances followed the sequence of H2 > CO2 > N2 > CH4 > C3H6, and showing good ideal selectivities for hydrogen recovery.

ZIF-8 membrane separation performance

◆ **Binary gas separation test of C_3H_6/C_3H_8 mixture**

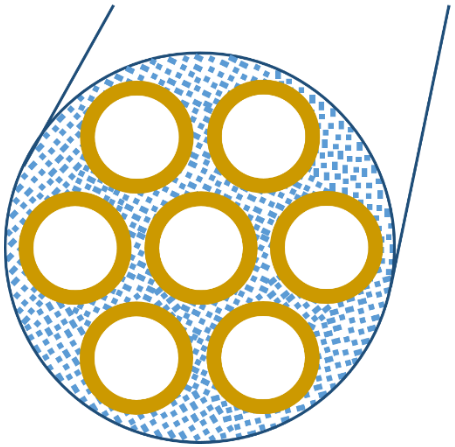


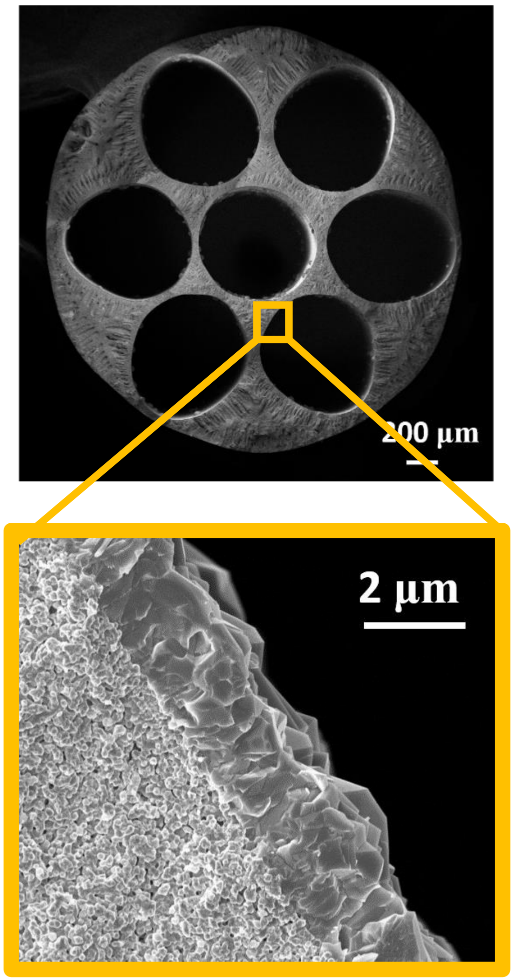
outstanding propylene/propane mixture gas separation factor with the maximum valve, about 140, by testing over 120 hours

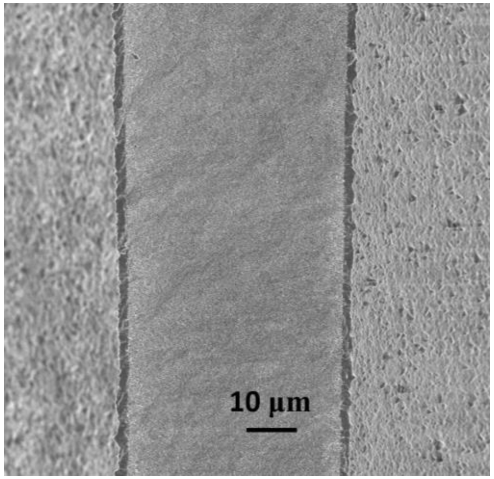
K Huang, **K Li**, et al., *Adv. Mater. Interfaces*, 2018, 1800287

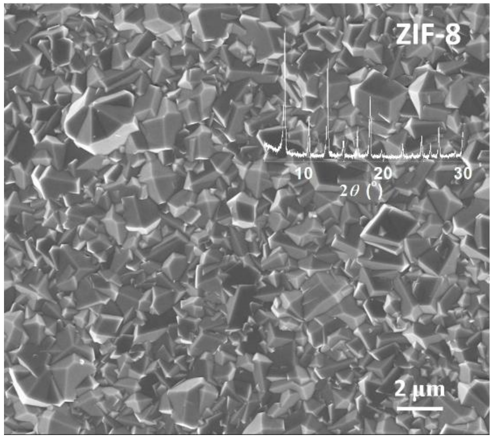
ZIF-8 membrane separation performance

- **7-bore YSZ micro-monolith supported inner ZIF-8 membrane**







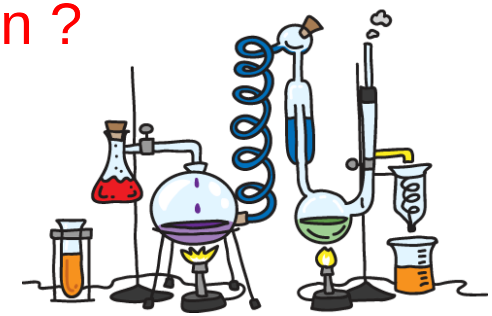


a good propylene/propane separation factor, around 30.

K Huang, **K Li**, et al., *Adv. Mater. Interfaces*, 2018, 1800287

Micropatterned MOF Membranes

Motivation ?

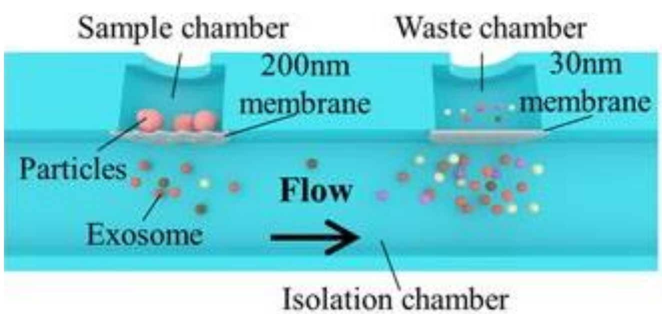


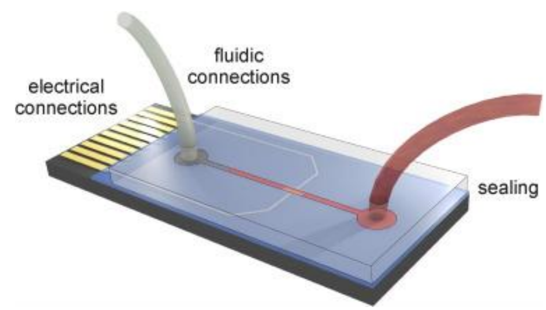
Laboratory scale

Scale-up (industry)

Available way:

- Incorporating MOF membranes into devices or instruments
- As a key role in a lab-on-a-chip device through miniaturization



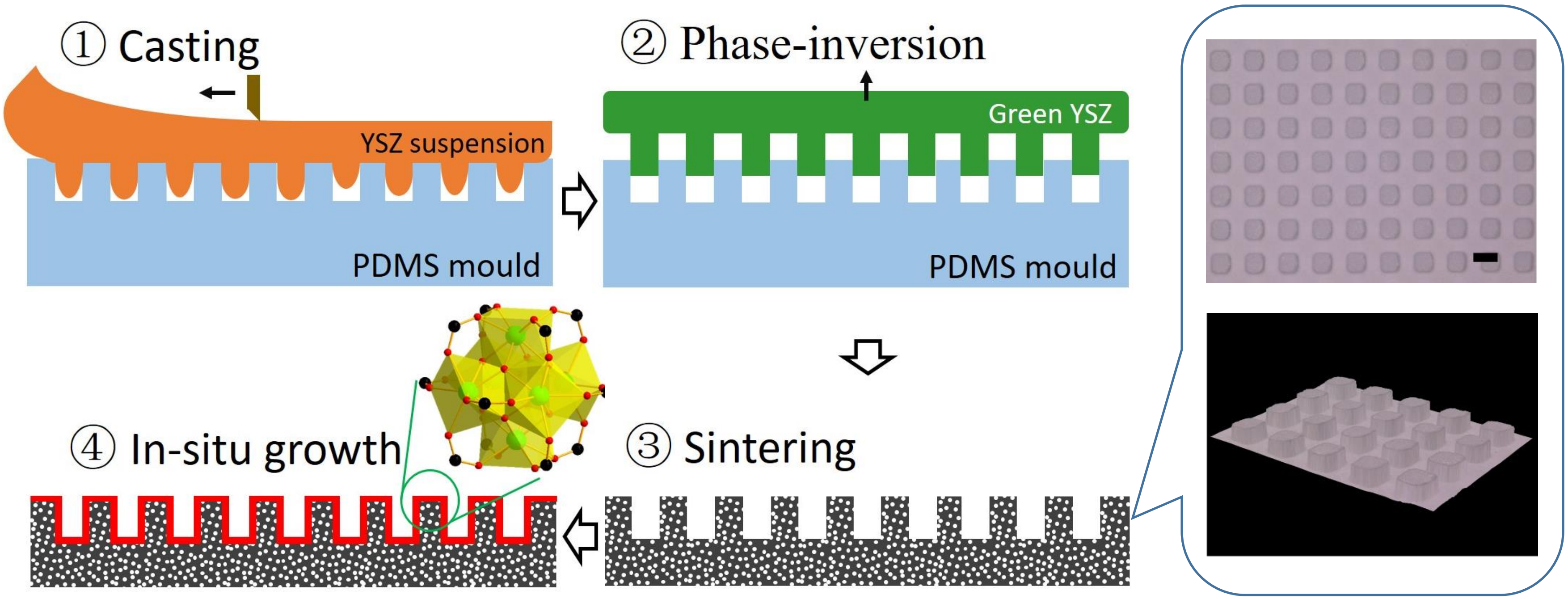


Target:

To demonstrate the feasibility of miniaturization of MOF membranes by patterning the membrane surface

Preparation of Micropatterned MOF Membranes

Bottom-up method to prepare Micropatterned MOF membranes



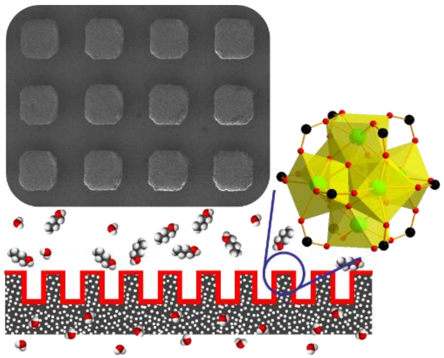
Schematic diagram of patterned YSZ ceramic substrates and UiO-66 membranes prepared

Array of cuboids
Length: ~75 um
Width: ~75 um
Height: ~32 um

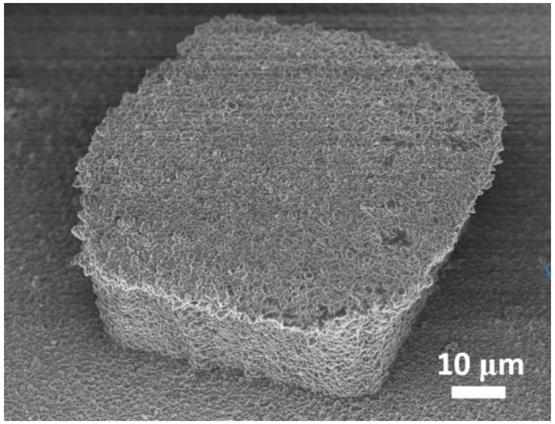
PDMS: polydimethylsiloxane
YSZ: yttria-stabilized zirconia (YSZ)

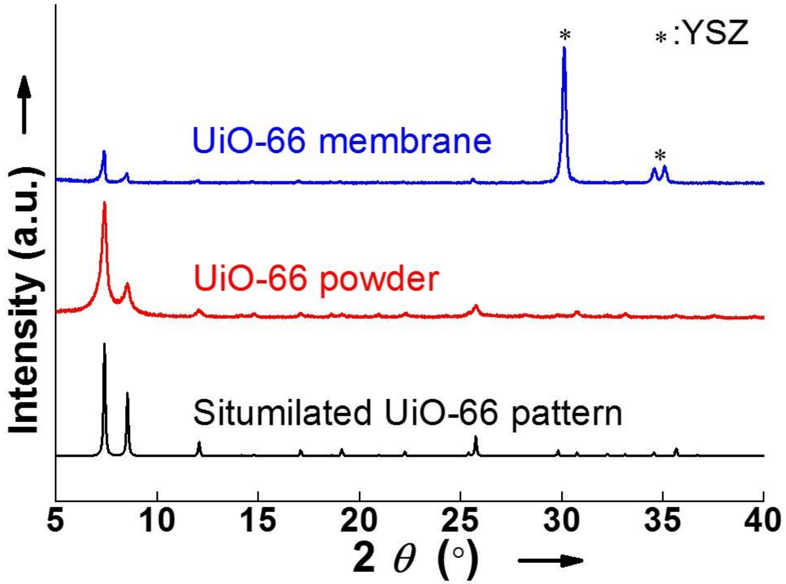
K Huang, **K Li**, et al., *Angew. Chem. Int. Ed.*, 2018, DOI: 10.1002/anie.201809872

Characterization

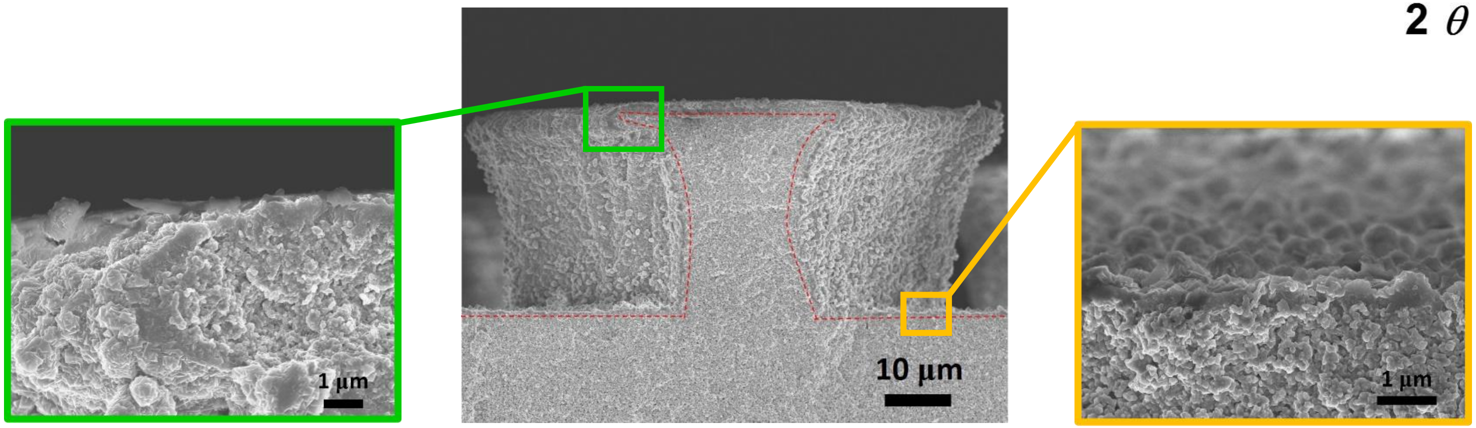


Surface SEM images





Cross-section SEM images

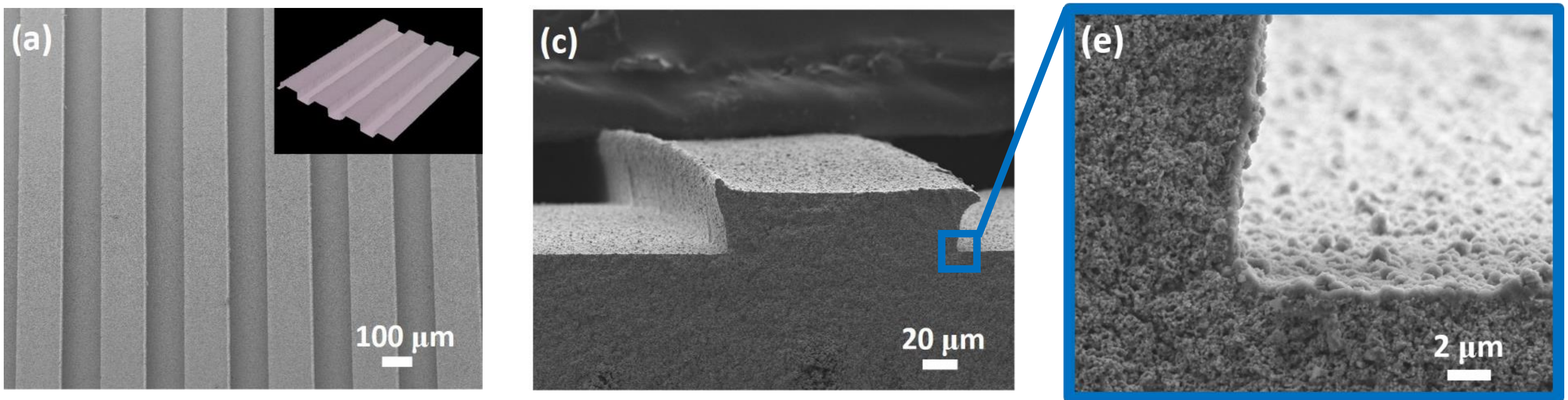


~900 nm (top parts)

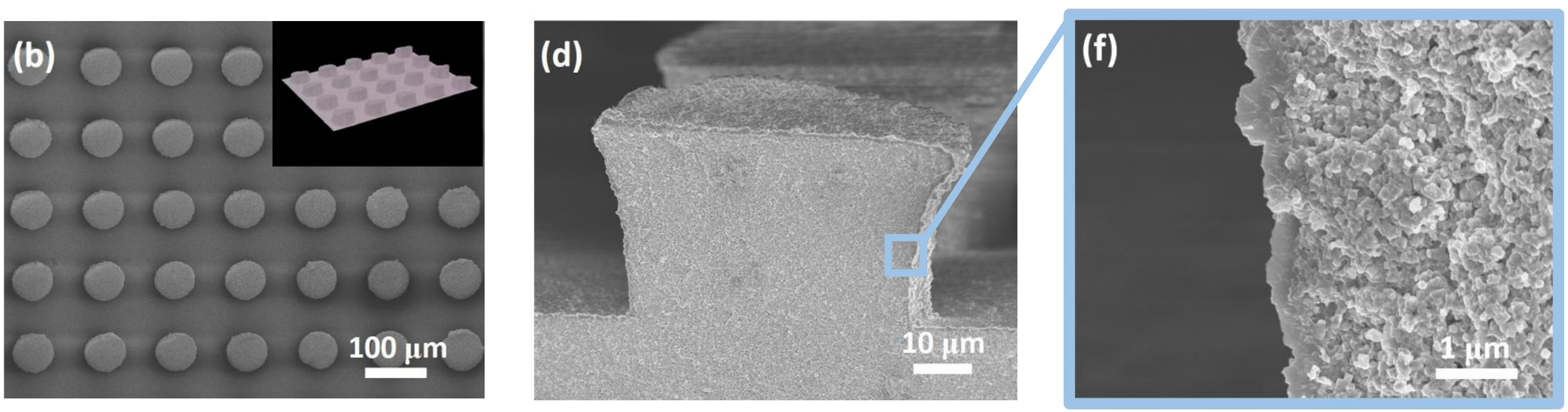
~300 nm (valley parts)

Characterization

◆ **Different features of the patterns**



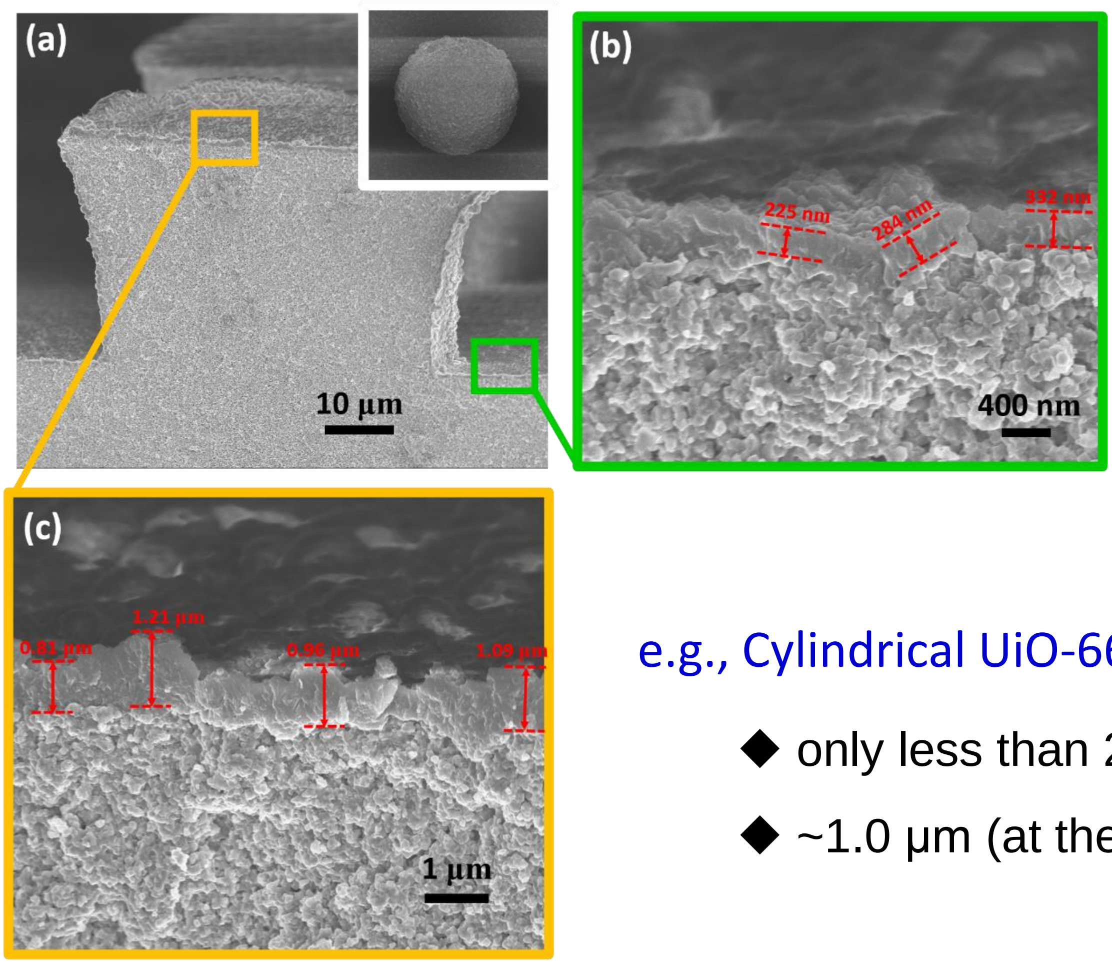
Channeled patterns



Cylindrical patterns

Micropatterned MOF Membranes

- **Membrane thickness**



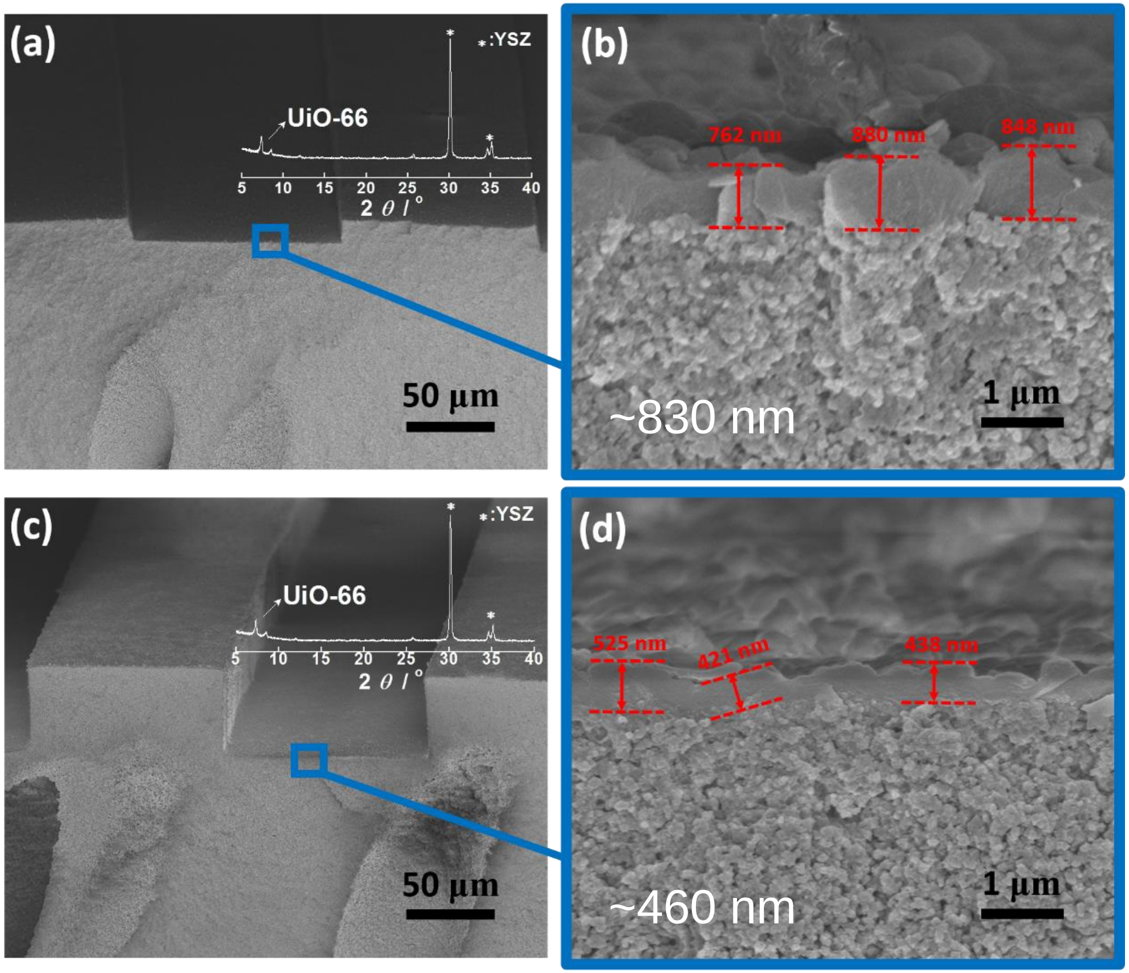
e.g., Cylindrical UiO-66 membranes:

- only less than 250 nm (at the valleys)
- ~1.0 µm (at the top of the cylinders)

➡ Such a trend can be attributed to the concentration profile of reactants over the patterned surface during the in-situ hydrothermal synthesis process.

Micropatterned MOF Membranes

- **Membrane thickness**



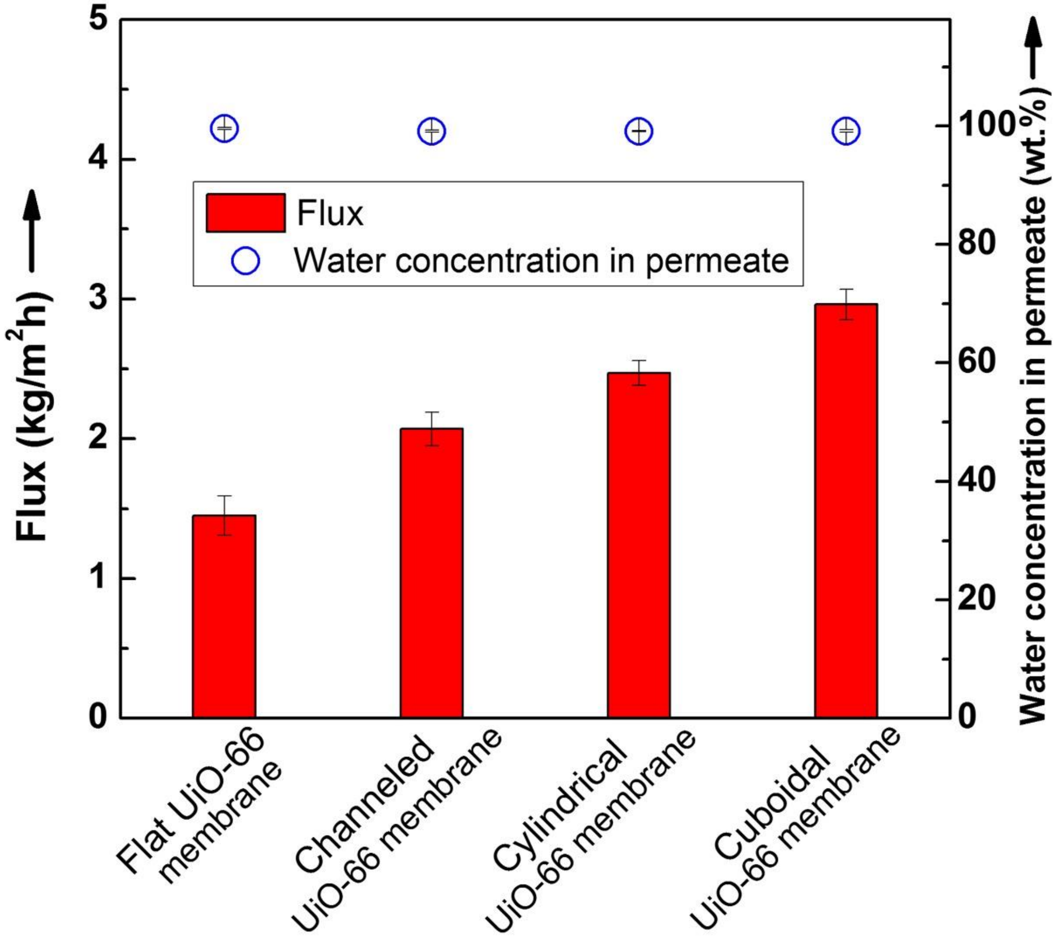
SEM images of two channeled UiO-66 membranes with different depth:

(a, b) 10 μm;

(c, d) 50 μm.

Micropatterned MOF Membranes

◆ **Separation performance of UiO-66 membranes with different patterns.**



Organic solvent dehydration:

10 wt.% water/n-butanol

✓ above 99 wt.% in the permeate

✓ separation factor of over 1,000

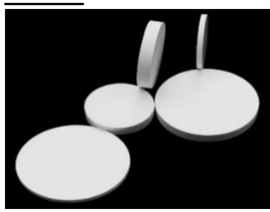
➢ equal quality with the unpatterned membrane

➢ considerably higher flux than the unpatterned membrane

Conclusions

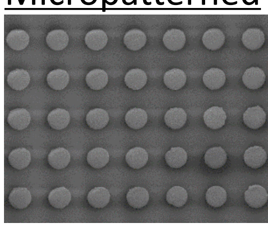
Ceramic supports

Disc



Hollow Fibre

Micropatterned



MOF materials

- $[Ni_2(L\text{-}asp)_2(bipy)]$ (Ni-LAB)
- $[Zn_2(cam)_2dabco]$ (Zn-CD)
- ZIF-67
- ZIF-8
- ZIF-71
- UiO-66

Applications

Chiral separation

Gas separation

- H_2 recovery
- CO_2 capture
- C_3H_6/C_3H_8

Bio-ethanol recovery

Dehydration organic solvent

MOFs are very promising materials for the membrane separation fileds

Thanks for Your Attention!

BRITISH COUNCIL
RESEARCHER LINKS

Newton Fund

BRITISH COUNCIL
英国文化教育协会
英国大使馆文化教育处

Barrer Centre

EPSRC
Engineering and Physical Sciences Research Council

国家自然科学基金委员会
1986
NATIONAL NATURAL SCIENCE FOUNDATION OF CHINA

Imperial College London