



Structural adjustment of mixed matrix membranes for CO₂ separation

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Contents



- **Background & Recent development**
- **Our research work**
- **Future direction**



Background & Recent development

Mixed matrix membranes (MMMs) offer a number of benefits in CO₂ separation



Common Form

Continuous phase: Polymer

- Break the performance limit
- **Good processability**

eg. Polyethylene Oxide (PEO)

Poly(vinylamine) (PVAm)

Disperse phase: Fillers

- Avoid brittleness
- **Excellent gas separation property**

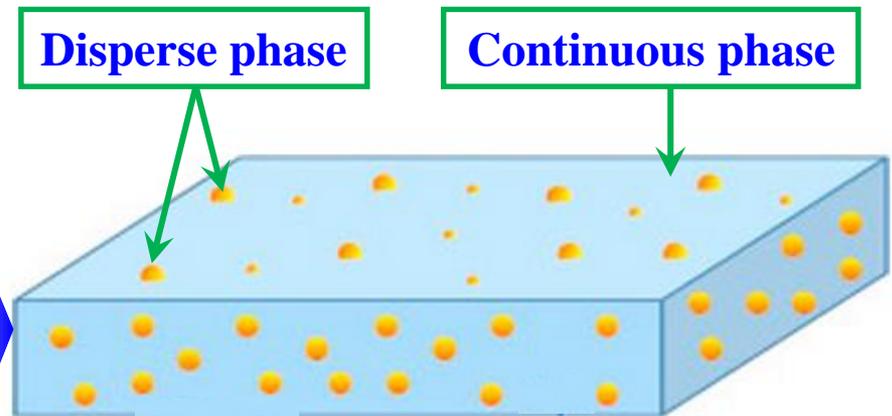
eg. Solid fillers: SiO₂

Porous fillers:

Metal-organic frameworks (MOFs)

Covalent Organic Frameworks (COFs)

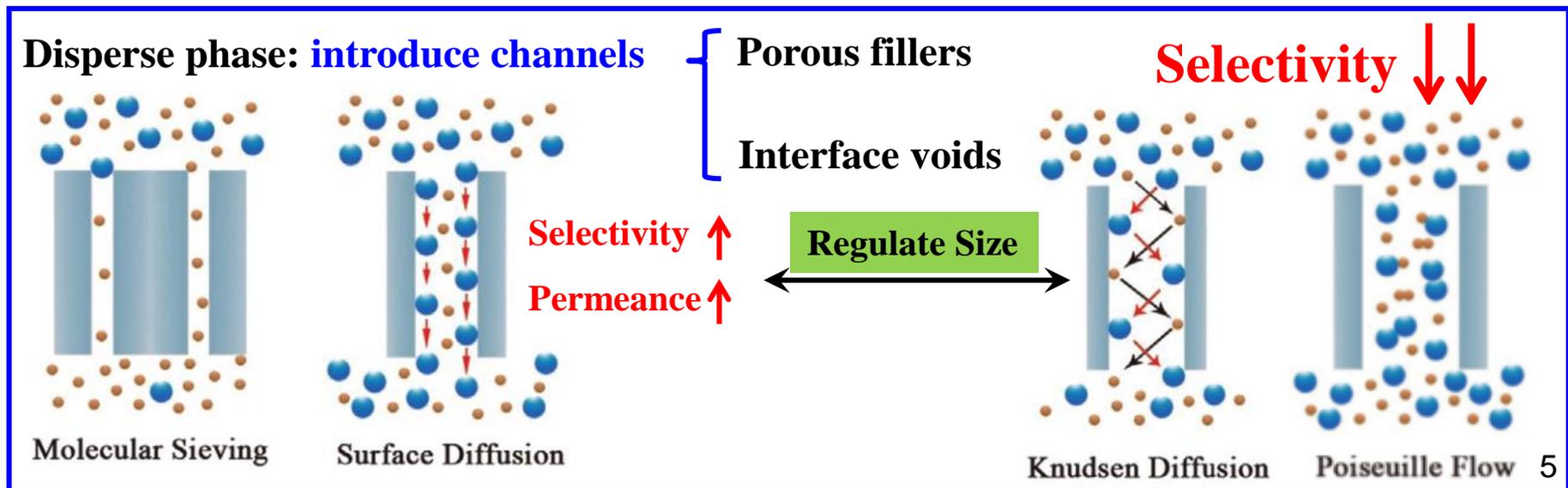
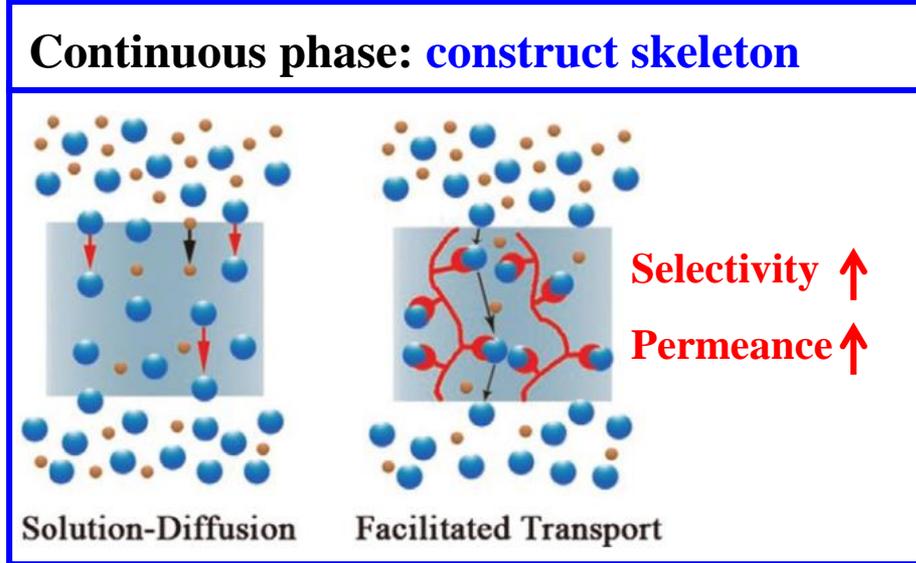
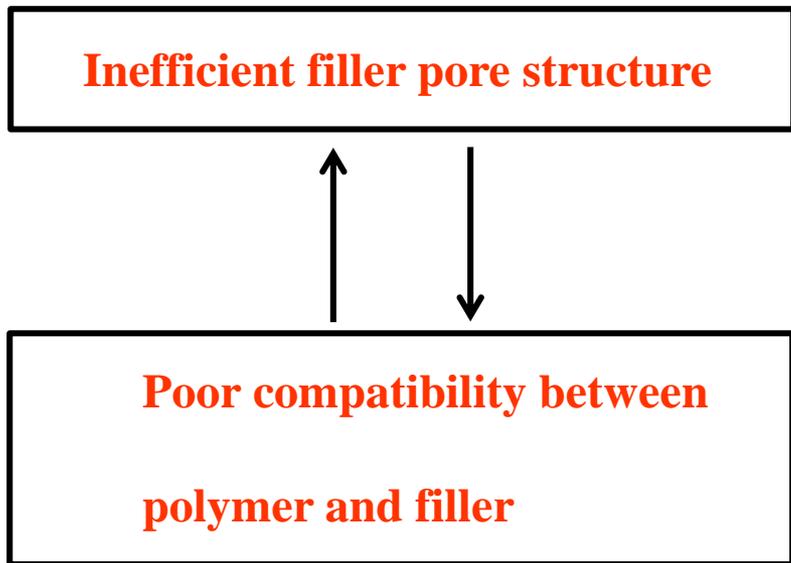
MMMs are blending of two phases:



✓ Circumvent Disadvantages

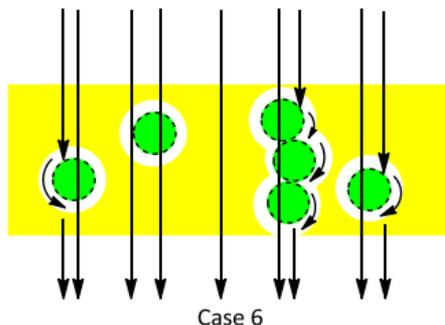
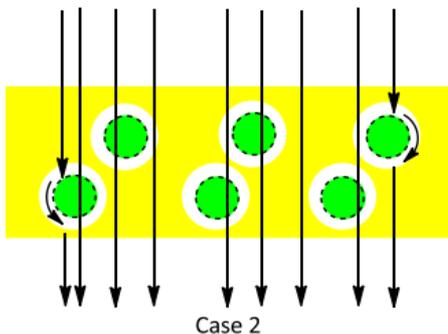
✓ Combine Advantages

Key problems of existing MMMs



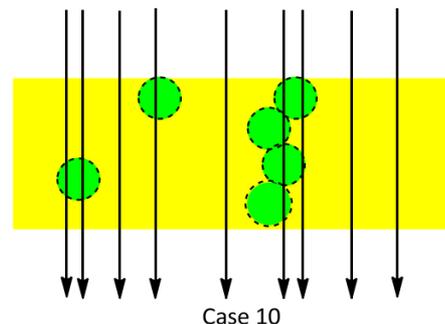
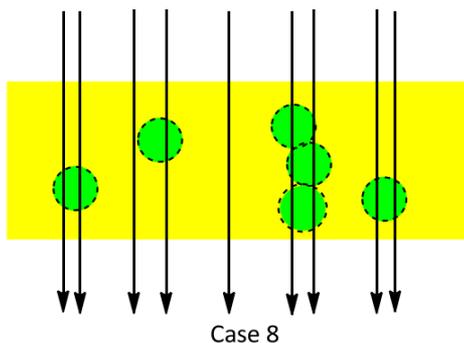
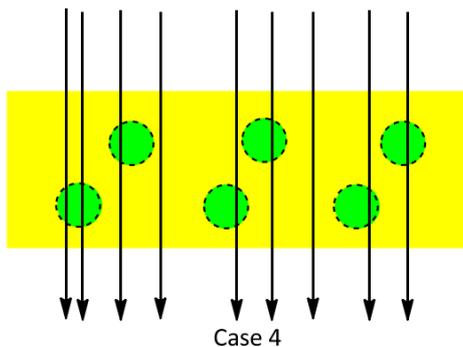
Porous fillers
Interface voids

Ideal morphology of MMMs



Target: Appropriate voids size, moderate compatibility

Not easy to control



Target: Appropriate pore structure of nanofiller + Good compatibility

Common strategies to enhance interfacial compatibility



➤ Silane coupling

Organosilane reacts with **hydroxyl groups** on the **filler surface** to **form bridges** between fillers and matrix.

➤ Grignard treatment ---- growing **whisker $Mg(OH)_2$** on the filler surface to create **roughened filler surface** to **promote interface adhesion** via **a series of physical changes**.

➤ Grafting ---- grafted with low molecular weight polymer with **EO or amine groups**.

Hydrogen bonding can be form between polymer and modified filler.

➤ Polymer functionalization

Functionalized polymer can **interact** with functional groups containing filler.

➤ In situ polymerization

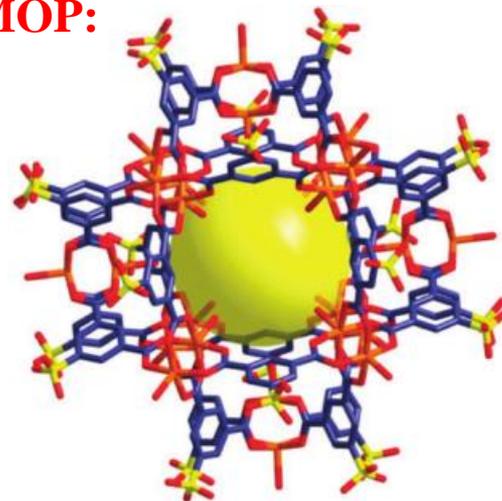
The filler **participate in** the polymer **synthesis**. **Chemical bonding** can form between polymer and filler.

➤

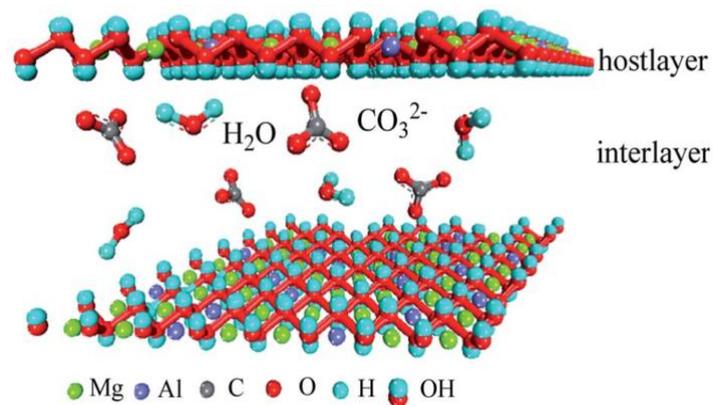
Common fillers with regulable pore structure

- ✓ Zeolite
- ✓ Graphene oxide (GO)
- ✓ Metal-organic frameworks (MOFs)
- ✓ Metal-organic polyhedra (MOPs)
- ✓ Covalent organic frameworks (COFs)
- ✓ Hydrotalcite (HT)
- ✓ Montmorillonite (MT)
- ✓

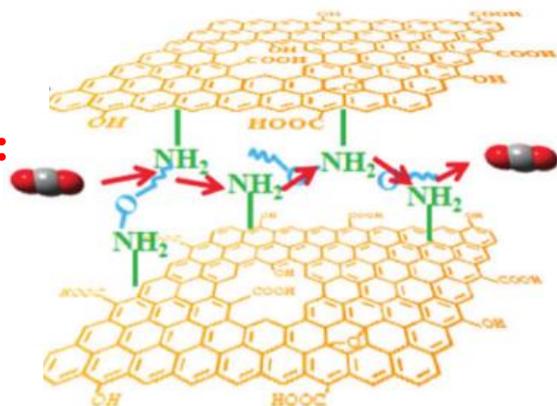
MOP:



HT:



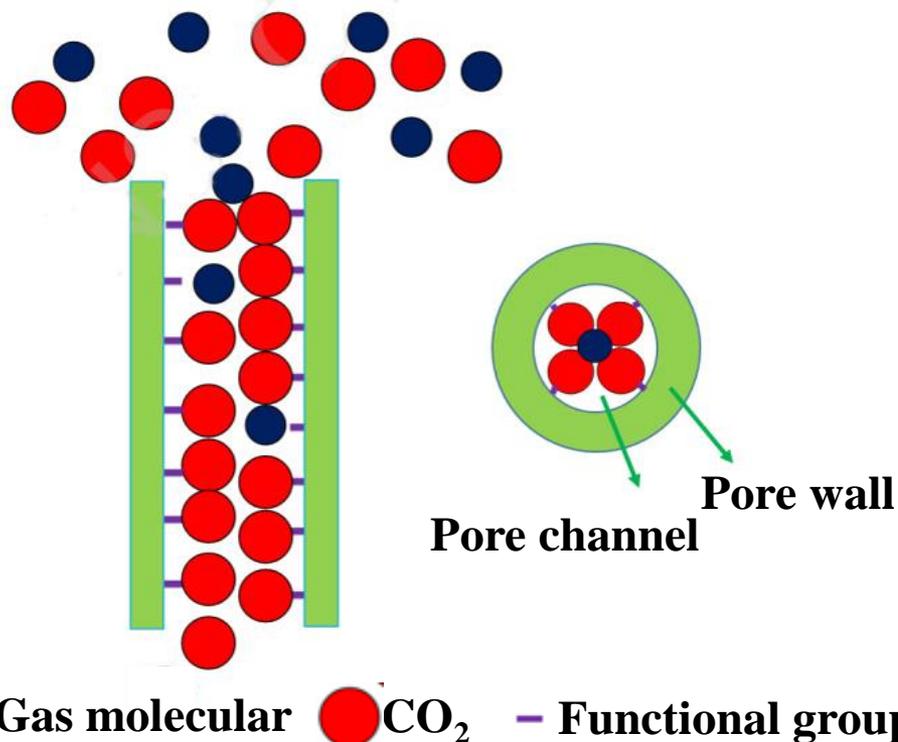
GO:





Our research work

Ideal CO₂ separation pore channels



Characteristics of ideal pore channels

Introduction of **functional groups** of CO₂ affinity

$$2D_{\text{CO}_2} < \text{pore size} < 2D_{\text{CO}_2} + D_{\text{gas molecular}}$$

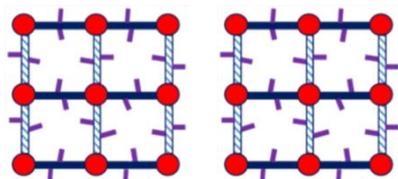
(6.60Å)

CO ₂ /H ₂ :	9.49Å
CO ₂ /N ₂ :	10.24Å
CO ₂ /CH ₄ :	10.40Å

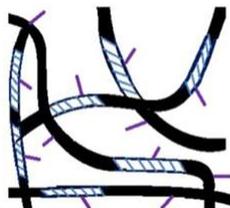
- CO₂ affinity functional groups can guarantee the **preferential adsorption** for CO₂ molecules. Besides, the **pore size** can only allow CO₂ molecules to pass through the pore by following **monomolecular surface diffusion mechanism**.
- Meanwhile, the CO₂-adsorbed pores were smaller than the other gases, **which blocked the other gases** and **enhanced the membrane selectivity**.

Design project

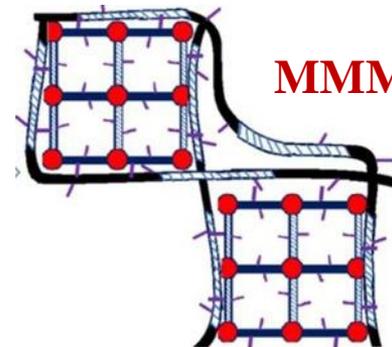
Porous materials



Polymer



MMMs



Amounts of functional groups on the pore walls



Increase the amount of CO₂ absorbed

Excellent pore channels



monomolecular surface diffusion

Crosslinking network structure



Outstanding mechanical property

Functional groups of CO₂ affinity



Highly interfacial compatibility

Improve the absorption of CO₂ in membrane

Two methods to develop high-performance MMMs for CO₂ separation



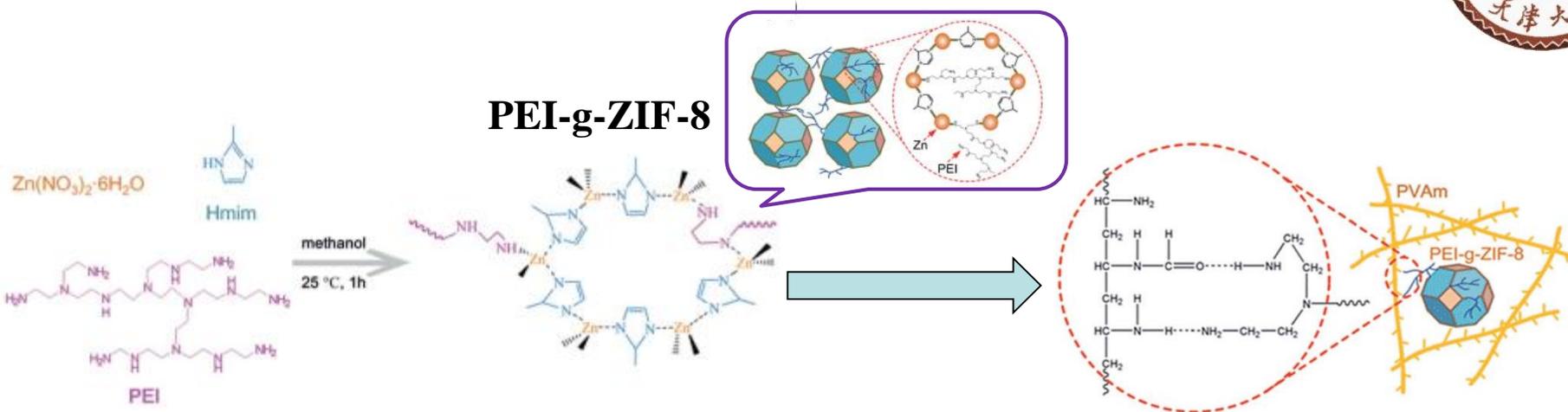
Grafting MOFs with polymers to regulate MOFs pore size and enhance the interfacial compatibility simultaneously.

Constructing vertical transfer channels with modified montmorillonite layers.

Improving interfacial compatibility and introducing high-speed channels for CO₂ separation membranes

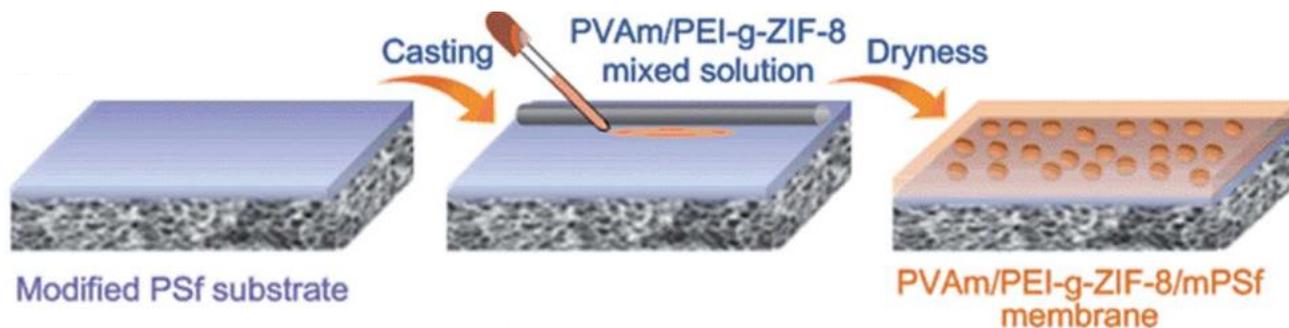
High-performance MMMs

In situ synthesis of polymer grafted ZIFs and application in mixed matrix membrane for CO₂ separation



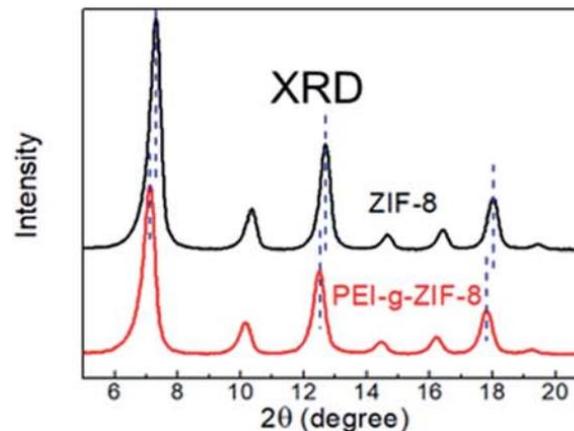
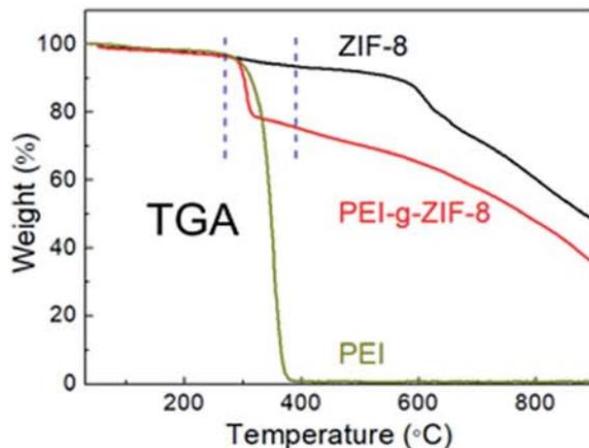
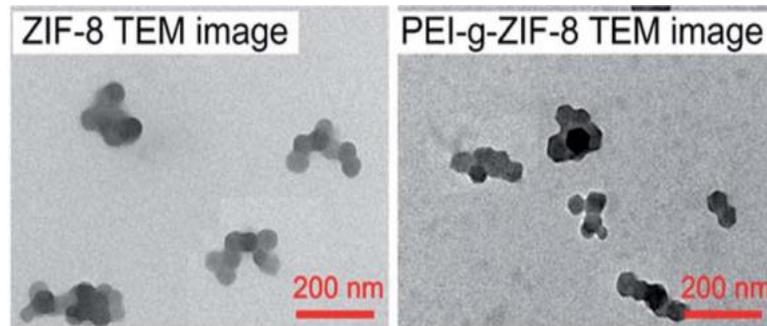
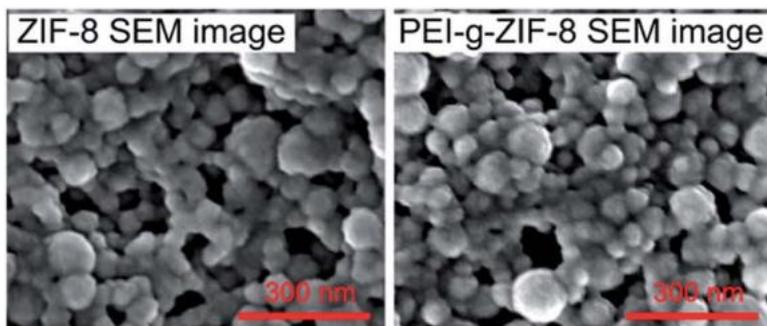
- **Enhancement** of pore channels
- **Modification** of hydrophilicity
- **Introduction** of more **amino groups**

- **Better interfacial compatibility**
- **Introduction** of more **functional groups**



- The strategy using **in situ synthesized polymer grafted metal organic frameworks (PEI-g-ZIF-8)** enhances **interfacial compatibility** and optimizes the pore structure.

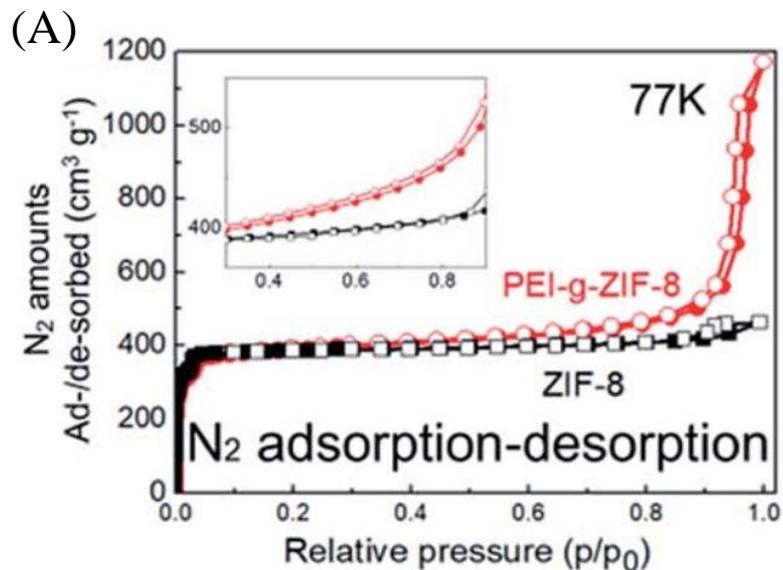
Characterization of PEI-g-ZIF-8 nanoparticles



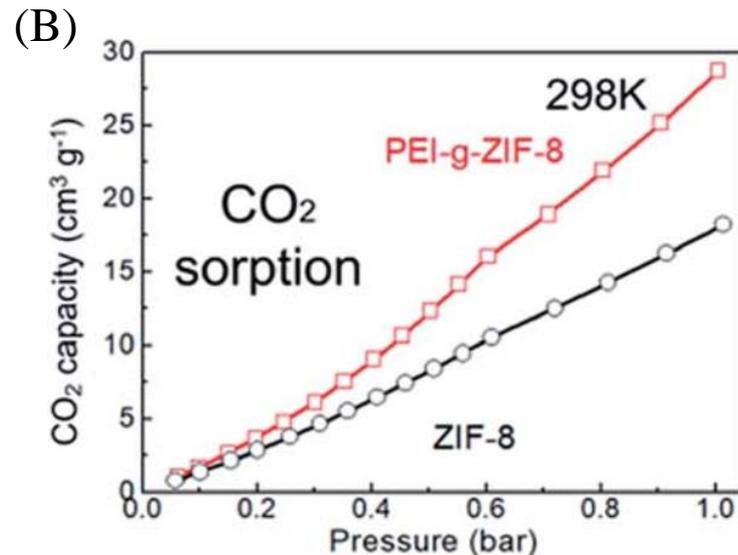
- There was **no obvious morphologic difference** between ZIF-8 and PEI-g-ZIF-8 nanoparticles.
- It was calculated that PEI accounted for **14.40 wt%** of PEI-g-ZIF-8 particles from TGA.
- The peaks of PEI-g-ZIF-8 particles were **weaker and shifted left** compared with ZIF-8, caused by the **crystallinity decrease**.



Characterization of PEI-g-ZIF-8 nanoparticles



N₂ adsorption-desorption isotherms of ZIF-8 and PEI-g-ZIF-8 nanoparticles



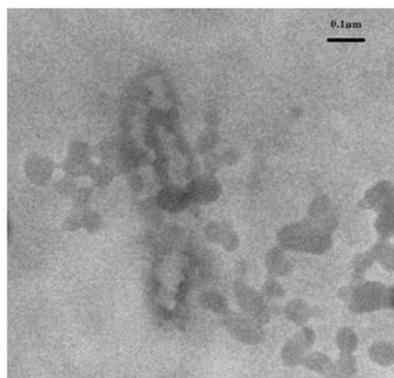
CO₂ sorption isotherms of ZIF-8 and PEI-g-ZIF-8 nanoparticles.

Table 1 Porous structure parameters of ZIF-8 and PEI-g-ZIF-8 nanoparticles

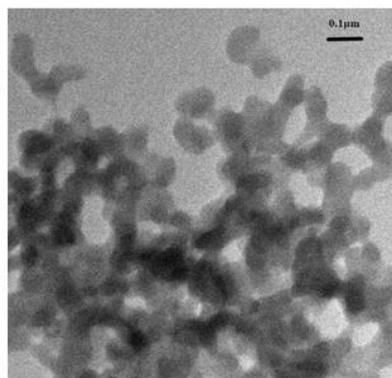
Sample	BET surface area (m ² g ⁻¹)	Langmuir surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Micropore diameter (nm)
ZIF-8	1503	1707	0.716	0.730
PEI-g-ZIF-8	1666	1856	1.676	0.753

- Compared with ZIF-8, PEI-g-ZIF-8 nanoparticle had a significant increase of **CO₂ sorption** and its **pore diameter** expanded from **0.730 nm** to **0.753 nm**.

Characterization of films and membranes



TEM image of PEI-g-ZIF-8



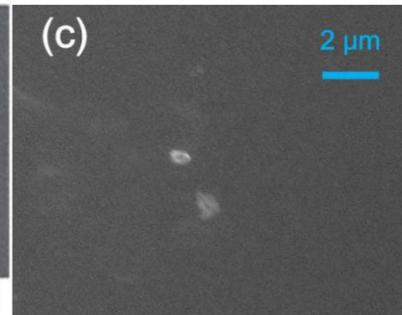
TEM image of ZIF-8

zeta potential of particles in pure water

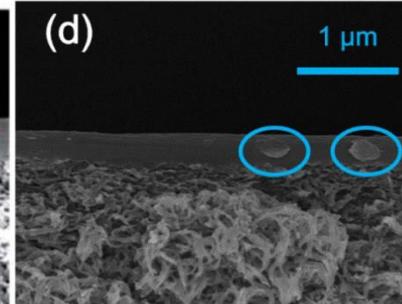
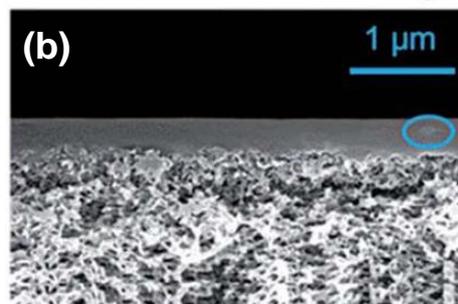
PEI-g-ZIF-8: $42.4 (\pm 0.2)$ mV

ZIF-8: $17.5 (\pm 0.2)$ mV

Surface SEM image



Crosssection SEM image



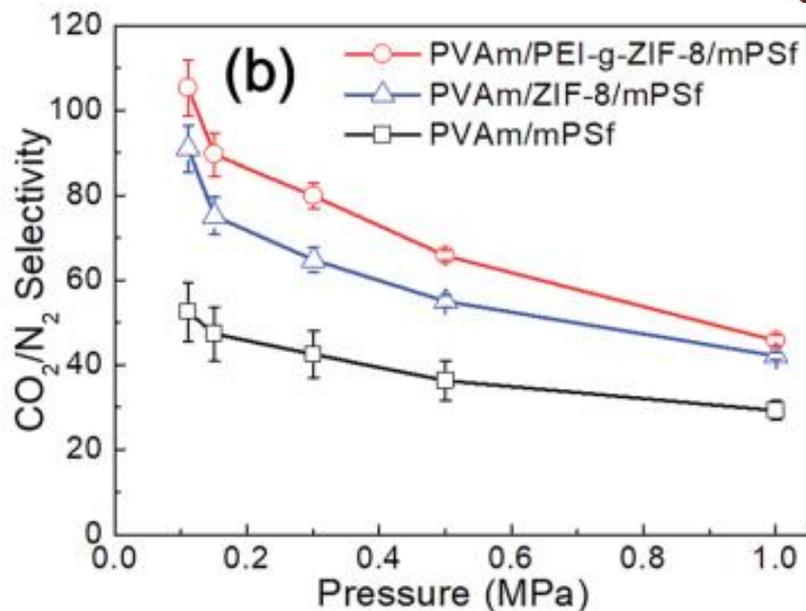
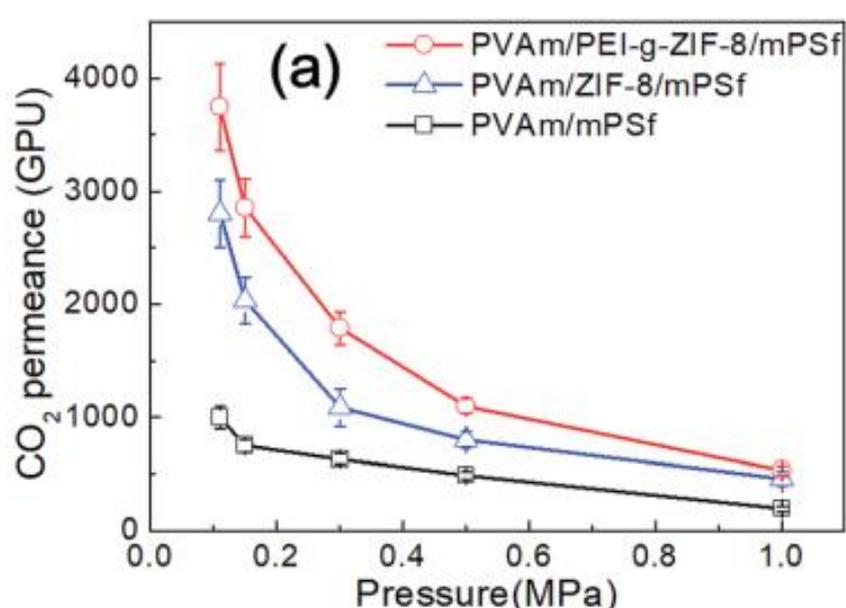
(a, b) PVAm/PEI-g-ZIF-8/mPSf membrane

(c, d) PVAm/ZIF-8/mPSf membrane

wet coating thickness: 100 μm, MP_{NPs} : 20.0 wt% (MP refers to mass proportion, NPs refers to nanoparticles)

- Compared with ZIF-8, PEI-g-ZIF-8 particles maintain **better dispersion and stability in aqueous solution**.
- The thickness of the membrane separation layer was generally **330 nm**.
- PVAm/ZIF-8/mPSf membrane showed severe **agglomeration** compared with PVAm/PEI-g-ZIF-8/mPSf membrane.

Effects of the incorporated nanoparticles on gas separation performance

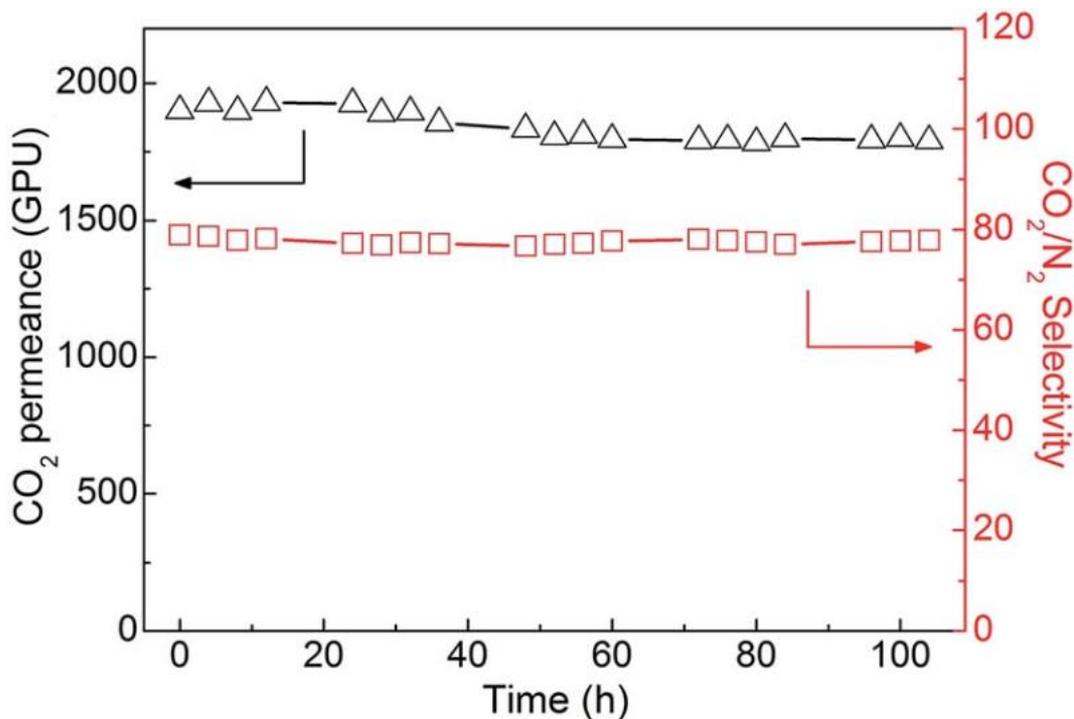


CO₂ permeance (a) and CO₂/N₂ selectivity (b) of different MMMs based on mPSf substrates tested with CO₂/N₂ (15/85 vol%) mixed gas;

- The PVAm/PEI-g-ZIF-8/mPSf membranes had an increase of **67.8%** in **CO₂ permeance** and an increase of **23.3%** in **CO₂/N₂ selectivity** over PVAm/ZIF-8/mPSf membranes under a feed gas pressure of **0.30 MPa**.
- The PEI-g-ZIF-8 nanoparticles presented an **outstanding porous structure** to enhance gas diffusion, and PEI chains provided **more amino groups as fixed carriers**.



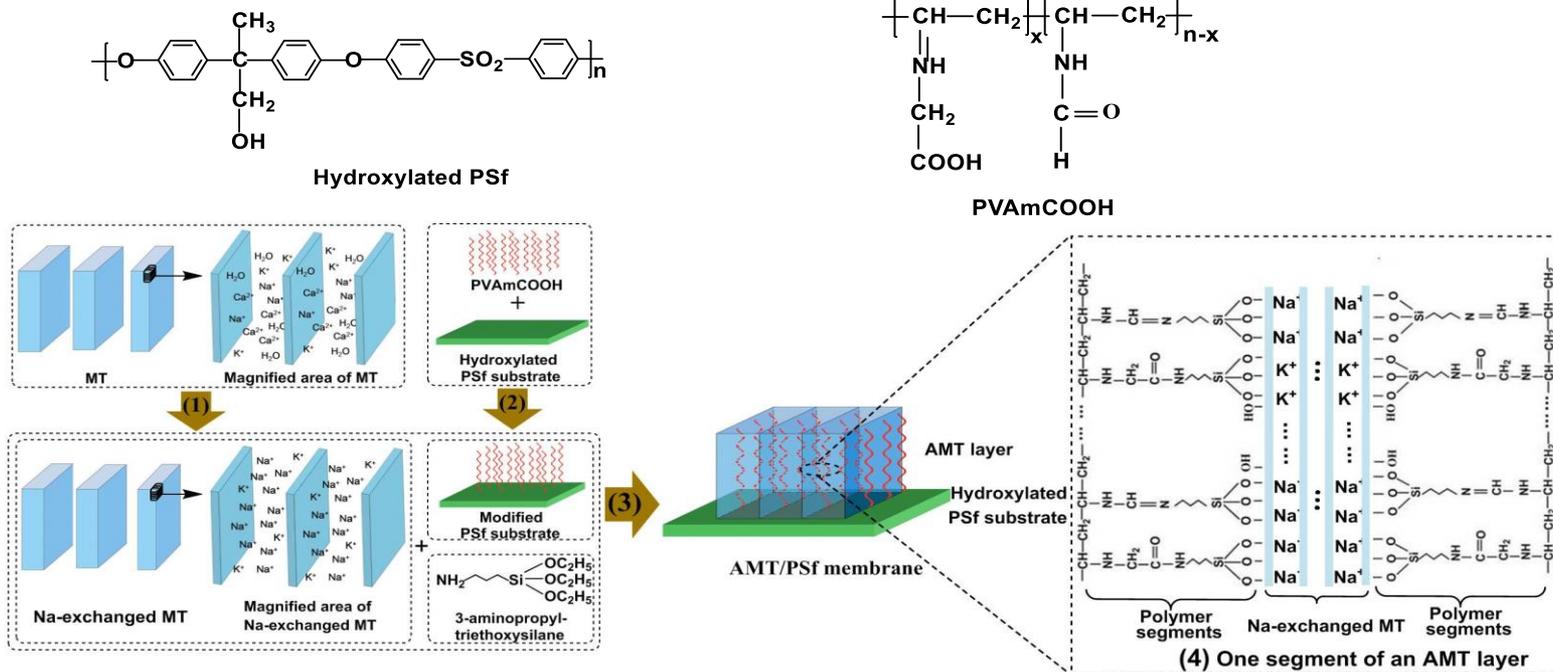
Performance stability of PVAm/PEI-g-ZIF-8 MMMs



Stability of the PVAm/PEI-g-ZIF-8/mPSf membrane for up to 100 h continuous separation. MP_{NPs} : 16.7 wt%. Feed gas: CO₂/N₂ (15/85 vol%) mixed gas. Feed gas pressure: 0.30 MPa.

- The **PVAm/PEI-g-ZIF-8/mPSf membrane** exhibited excellent separation stability during the **100 h continuous gas permeation test**.

Modifying MT and crosslinking it with modified PSf substrate to get vertical CO₂ transfer channels



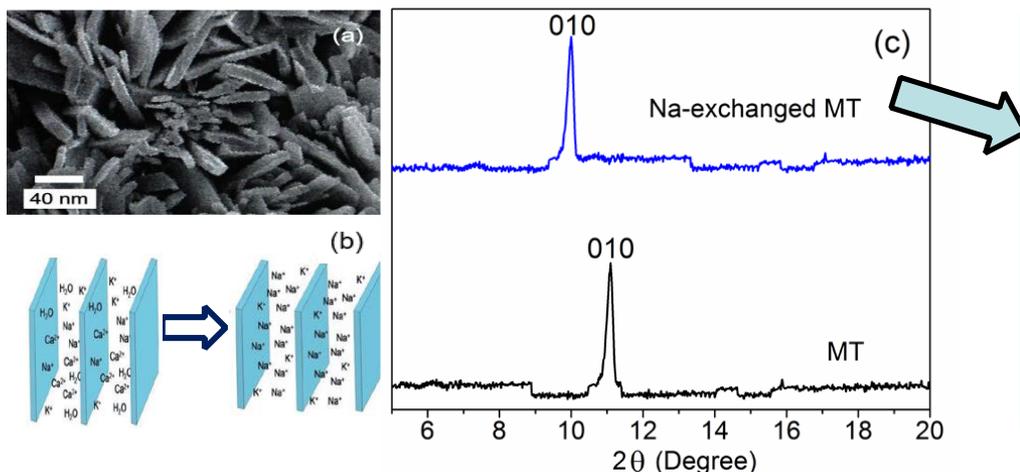
- Highly permeable **montmorillonite layers** **bonded and aligned** with the chain stretching orientation of **polyvinylamineacid** were immobilized onto a porous **polysulfone** substrate to fabricate **aligned montmorillonite-polyvinylamineacid/polysulfone (AMT-PVAmCOOH/PSf)** mixed-matrix membranes for CO₂ separation.
- **High-speed gas-transport channels** were formed by the **aligned interlayer gaps (0.88nm)** of the modified montmorillonite, through which CO₂ transport primarily occurred.

Modifying MT



—Convert MT to Na exchanged MT to construct pore channels

- **Montmorillonite** had great potential to be utilized for CO₂ separation due to its suitable interlayer gaps (**0.713 nm**).
- To avoid **precipitation** of **Ca ions** in the presence of **hydroxy groups** (resided in the MT), **Na-exchanged MT** was synthesized.

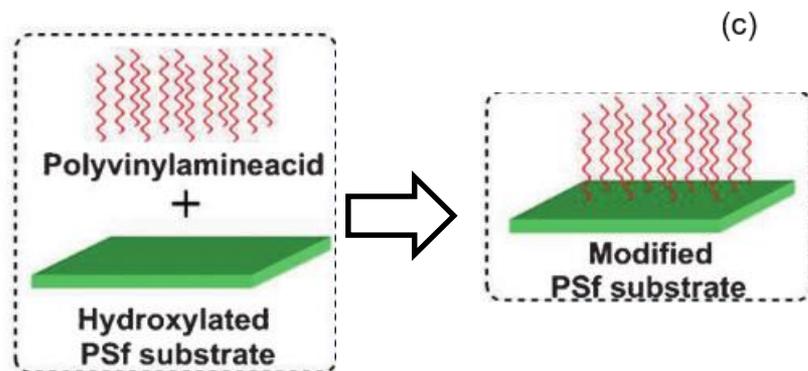
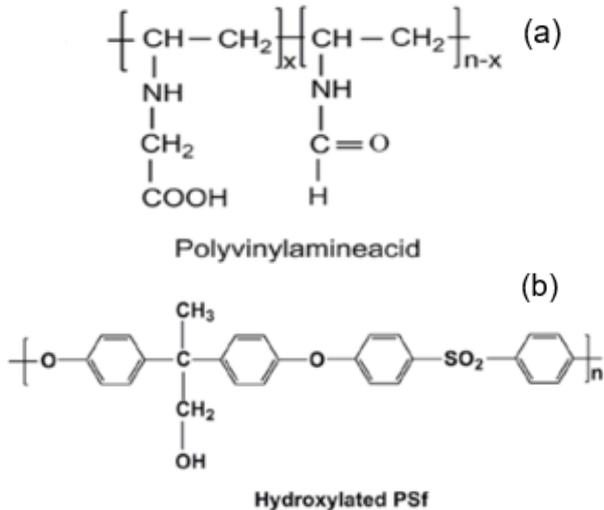


- The Na-exchanged MT interplay space is calculated from its **reflection angel** in the XRD characterization by using **Bragg's equation**.
- **Interlayer gaps**: from **0.713 nm** to **0.88 nm**.

(a) SEM surface image of Na-exchanged MT (b) Na ion exchange to form Na-exchanged MT (c) XRD spectra of MT and Na-exchanged MT confirming crystallinity.

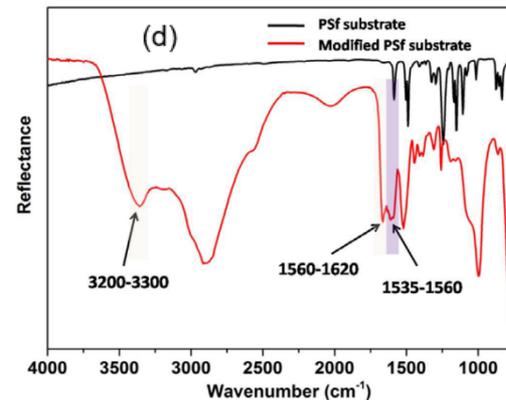
- **Successful synthesis** of Na-exchanged MT was confirmed by a series of characterization methods.
- Na-exchanged MT had **average cuboid shape** of about **100nm × 40nm × 10nm** and appropriate width of the **interlayer gaps** (**0.88 nm**), which were supposed to be an ideal pore channels for CO₂ preferential penetration ($2D_{CO_2} < 0.88nm < 2D_{CO_2} + D_{gas\ molecular}$).

Grafting hydroxylated PSf substrate with polyvinylamineacid



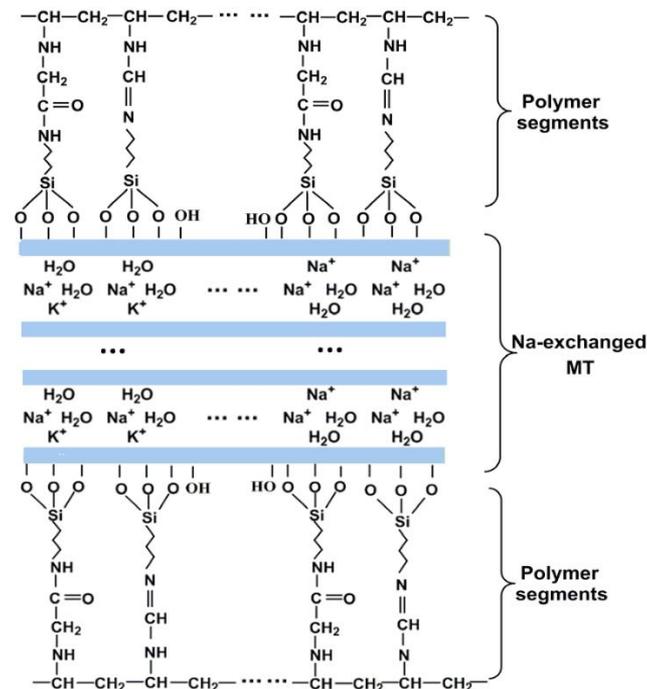
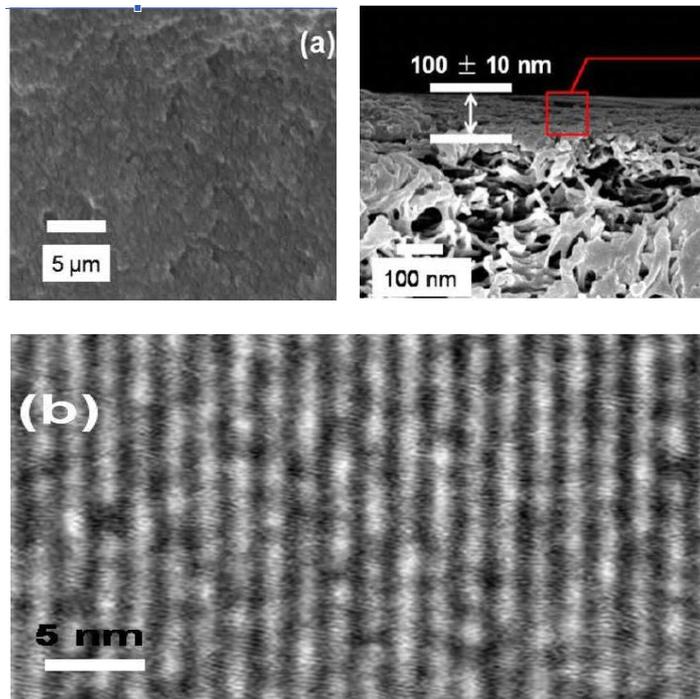
➤ ATR-FTIR spectra showed that **modified PSf substrate** grafted with **polyvinylamineacid** (continuous phase of) was **successfully synthesized**.

➤ In thionyl chloride solvent, polyvinylamineacid chains may be **stretched or uncoiled**, because thionyl chloride converts carboxylic acid groups in polyvinylamineacid to acyl chlorides, reducing the overall amount of and hydrogen bonding.



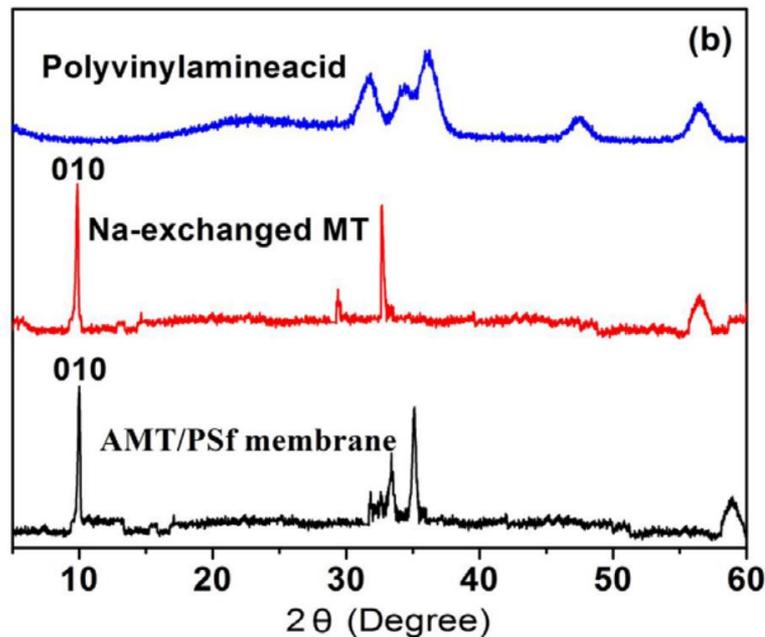
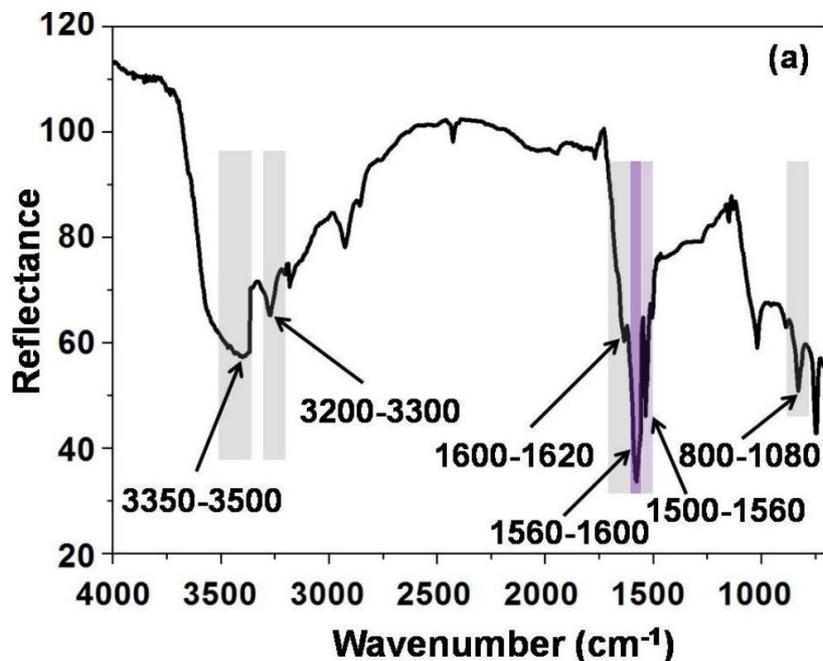
(a) Polyvinylamineacid (b) modified PSf substrates (c) surface modification process (d) Comparative ATR-FTIR spectra of PSf and modified PSf substrates

Preparation of AMT-PVAmCOOH/PSf mixed-matrix membranes



- AMT-PVAmCOOH/PSf membranes were prepared by **immobilizing Na-exchanged MT** on the surface of **modified PSf substrates** by using **ethoxysilane coupling agent 3-aminopropyltriethoxysilane**. In the reaction process, the **curve distribution** of polyvinylamineacid in the **modified PSf substrate** was responsible for aligning the MT.
- **Defect-free MMMs** with a **thickness** of about **0.1 μm** and a **relative complete channels** were confirmed by **SEM and TEM**.

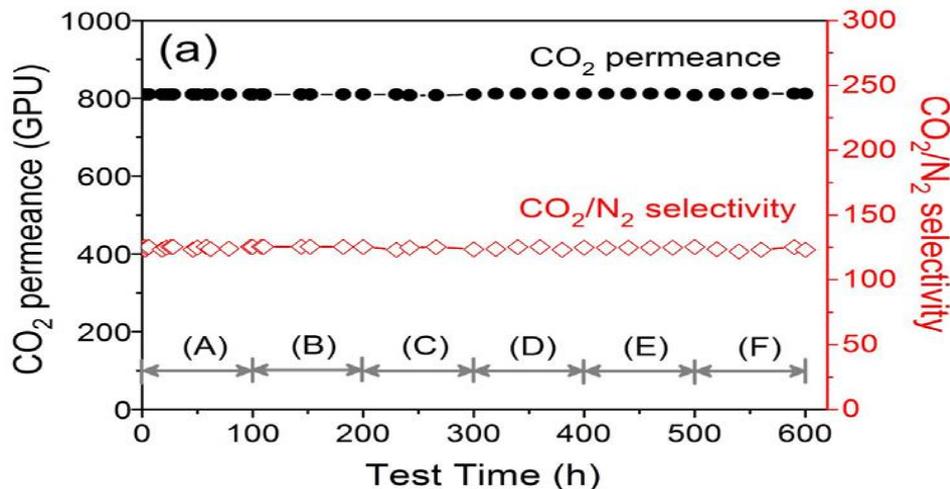
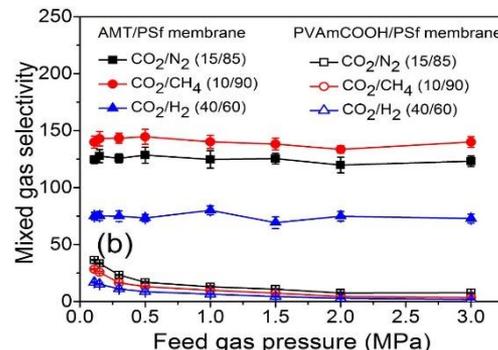
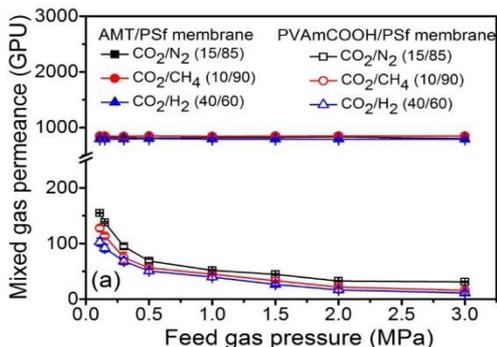
Characterization of the Membranes



(a) ATR-FTIR spectrum of AMT/PSf membrane, (b) Comparative XRD spectra of polyvinylamineacid, Na-exchanged MT and AMT/PSf membranes.

- From the XRD spectra, it was clear that the reflection angel in AMT-PVAmCOOH/PSf membranes was similar to that of Na-exchanged MT, which indicated AMT interlayer space of 0.88 nm.
- In all, combined with the characterization of TEM, it could conclude that we successfully synthesized montmorillonite-polyvinylamineacid/polysulfone mixed-matrix membranes with vertical CO₂ transfer channels of 0.88 nm.

AMT-PVAmCOOH/PSf mixed-matrix membranes show excellent gas separation performance and stability



➤ The resulting **AMT-PVAmCOOH/PSf** membranes displayed **high permeance** and **selectivities of CO₂**.

➤ AMT-PVAmCOOH/PSf membranes were **stable** over a period of **600 h** and their performance was **independent with feed pressure**.



Conclusions 1

- We put forward a strategy of using in situ synthesized polymer grafted metal organic frameworks to optimize the pore structure and enhance interfacial compatibility in MMMs.
- ✓ With the introduction of PEI molecules, the PEI-g-ZIF-8 nanoparticles presented better porous structure, amino functionalized surface, and improved interfacial compatibility with the PVAm matrix.
- ✓ The MMMs composed of PEI-g-ZIF-8 and PVAm showed high CO₂ permselectivity.



Conclusions 2

- We constructed vertical transfer channels for high-speed CO₂ transport in MMMs using modified montmorillonite.
- ✓ With the Na ions exchange process, **interlayer precipitation was eliminated** and the **interlayer gap was expanded** from 0.713nm to 0.88nm.
- ✓ **The modified substrate** possessed **stretched** PVAmCOOH chains which acted as polymer matrix.
- ✓ Na-exchanged MT **bonded and aligned** with the polymer matrix to form **vertical transfer channels** for CO₂ transport.
- ✓ AMT-PVAmCOOH/PSf MMMs showed **excellent CO₂ separation performance and stability**.



Future Direction



- **Developing new polymers** with high permeability and selectivity.
- **Synthesizing new nanofillers** with suitable pore structure and particle size especially organic nanofillers that have interaction with CO₂ molecules.
- Investigating the relationship between interface morphology and gas transport property **systematically and qualitatively**.
- Exploring **new methods** to improve compatibility between polymer and filler, and **enhance** gas permselectivity of the MMMs simultaneously.
- Realizing **the industry-scale fabrication** and **application** of MMMs.



Others

➤ Non-MMMs:

- Membranes formed by polymer with **intrinsic microporosity** (eg. PIM)
- Membranes formed by **porous materials in large scale**

➤ Tolerance

- Accurate functional groups: increase the **tolerance of impurity**
- Increase **high-pressure** membrane performance
- Increase **high-temperature** membrane performance



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Thank You for your attention!

