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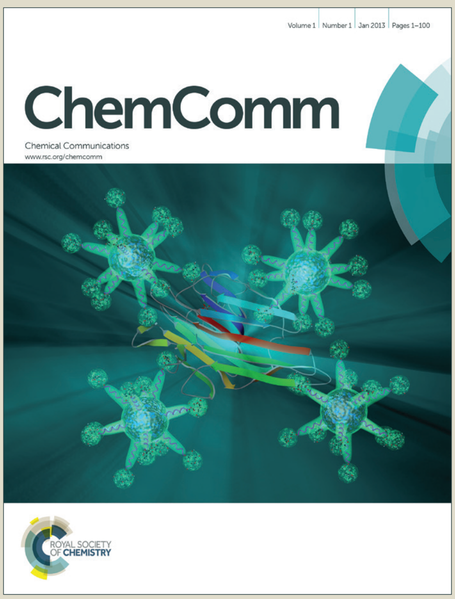

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ARTICLE TYPE

Synthesis of trinity metal-organic framework membranes for CO_2 capture

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Mixed-matrix membrane and MOF layer membrane were integrated to synthesize novel trinity MOF membranes by using different substrates such as polymeric hollow fiber membrane. The trinity membranes exhibited excellent performance for both H_2/CO_2 and N_2/CO_2 separation.

Metal-organic frameworks (MOFs) are porous hybrid organic–inorganic materials consisting of metal cations or metal oxide clusters bridged by organic linker molecules. As a new type of porous materials, MOFs have lots of applications in various fields such as chemical sensing, separation, drug delivery, fuel cell and catalysis.[1] It has been drawn widespread attention over the past decades.[2] Compared with the zeolites, MOFs have many unique properties, such as structural diversity and variety, high surface areas, framework flexibility, chemical variability, no template, fine-tuneable pore structures, good adsorption, selective adsorption and chemical functionalization, as well as the less energy intensive synthesis conditions.[3] Thus, MOF membranes have been greatly developed in the field of gas separation.[3] In previous studies, the gas separation MOF membranes are mainly divided into two kinds: mixed-matrix membranes (MMMs) and MOF layer membranes. For MMMs, the MOF crystals are blended into the polymers to form membranes. However, the void spaces between the MOFs and the polymeric matrix maybe displayed, thus the molecules can bypass the filler particles, and resulting in a loss of selectivity.[4] Meanwhile the mixed crystals are usually too small to provide an uninterrupted channel for gas to go through, so the improved amount of the permeance is often not obvious.[4b] Moreover, the separation performance of the membranes is generally controlled by the solution-diffusion model, which is unfit for some gas mixture separation, such as H_2-CO_2 mixtures. Since most polymer membranes show undesirable counterbalance characteristics of H_2-selective diffusivity and CO_2-selective solubility, the effective separation of H_2 and CO_2 mixtures is still an issue.[4b] For MOF layer membranes, the synthesis method is growing the MOF layers on a substrate. There are some papers reporting the successful synthesis of continuous MOF membranes by seeding, reactive seeding, covalent functionalization or contra-diffusion.[5] But the preparation of continuous and dense MOF membranes is always a big challenge.[5e] These membranes are proved to have successful separation of the gases whose kinetic diameters have great difference. While for some gases whose kinetic diameters are similar to each other, the separation performance turns to be not good. For example, in $Cu_3(BTC)_2$ and MOF-5 membranes, the separation factors for H_2/CO_2 can reach relatively high values, about 4.00-13.56, while for N_2/CO_2 or CO_2/N_2, the separation factors are relatively low, about 0.98-1.84 or 0.55-1.02. In respect to the ZIF membranes, the higher separation factors of H_2/CO_2 are usually in the range of 7.00 to 20.00 due to molecular sieving, but for N_2/CO_2, the selectivities are similarly low and drop in the range of 0.33~3.23 (see Tab. S1 ESI†).[5h] The biggest H_2/CO_2 separation factor can be obtained of 34.90 reported by Huang *et al.*, but the N_2 permeance over CO_2 was only 3.23 times.[5f] Therefore, we go forward to think if we can combine those two types of membranes to achieve an exceptional result.

Ge *et al*. used the polymer/zeolite mixed-matrix hollow fiber membranes as substrate to provide the anchor to the growth of zeolite layer, the prepared membrane had excellent pervaporation performance.[6a] But for MOF layer membrane, the MOF layer is often grown on inorganic substrates such as metal net, aluminium oxide and titanium dioxide. So far, there are few literatures concerning the growth of MOF layer on MMMs or polymer membranes.[5g, i, j],In our previous studies, we have made useful attempts to grow the continuous MOF layer on the PAN hollow fiber membrane successfully. As expected, the membrane obtained held a relatively high separation factor of 7.05 for H_2/CO_2.[6b]

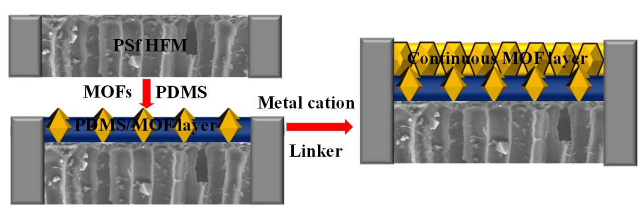

Fig. 1 Schematic of preparation of trinity membrane

Herein we integrated the MMMs and MOF layer membrane to fabricate a novel trinity MOF membrane, which had good separation performance for both H_2/CO_2 and N_2/CO_2. In order to increase the membrane surface area per volume, reduce the manufacturing costs and scale up easily,[6,7] the polymer hollow fiber membrane (HFM) was used as substrate. To provide uninterrupted channel for gases pass and increase the permeance, large MOF crystals were used to prepare the polydimethysiloxane (PDMS)/MOF layer. Up to now, there is no report on the growth of MOF layer on MOF MMMs, especially with the application of HFMs as substrate. The schematic is presented in **Fig. 1**. First, The MOF crystals were blended with PDMS, cross-linking agent, catalyst, and cyclohexane to stir for 4h, then the resultant solution was deposited onto polysulfone (PSf) HFM by drop coating (Fig. S1 ESI†). The mixture polymer/MOF layer has four main purposes: (i) serving as seeds for the growth of a continuous and well-intergrowth MOFs layer; (ii) increasing the adhesion of MOFs layer; (iii) enhancing the ability of gas separation and (iv) reducing the mass transfer resistance compared with entire MMMs or pure polymer layer. Second, the PSf hollow fiber substrate with polymer/MOFs layer was vertically immersed into the Teflon autoclave which was filled by mother solution to crystallize.

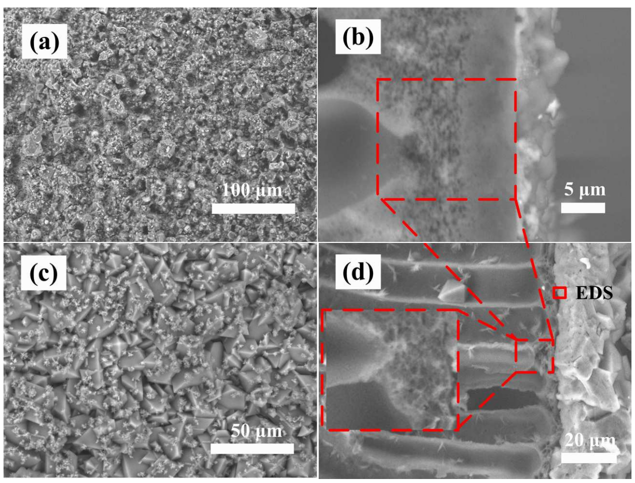

Fig. 2 Outer surface and cross-section SEM images of (a) (b) PSf HFM with PDMS/$Cu_3(BTC)_2$ layer and (c) (d) trinity membrane, respectively.

After successful synthesis of trinity membrane, the membrane was confirmed by various instruments. The FTIR spectra of original PSf HFM, PSf HFM with PDMS layer and PSf HFM with PDMS/$Cu_3(BTC)_2$ layer are displayed in Fig. S2 ESI†. The band at around 1013 cm^{-1} in the spectra of PDMS layer and PSf HFM with PDMS/$Cu_3(BTC)_2$ showed the existence of the cross-linked PDMS. Fig. S3 ESI† presents the XRD diffractogram of the liquid $Cu_3(BTC)_2$ powder. The XRD pattern of the $Cu_3(BTC)_2$ powder was similar to the previous studies, indicated the phase purity and homogeneity of the trinity membrane.[8] The morphology of the as-synthesized membranes was examined by SEM. It was found that PSf HFM was covered by a PDMS/$Cu_3(BTC)_2$ layer or dense PDMS layer (**Fig. 2**a and Fig. S4 ESI†). Fig. 2a and b indicate that the octahedral $Cu_3(BTC)_2$ crystals was not fully covered by the cross-linked PDMS. It is a good news for the synthesis of $Cu_3(BTC)_2$ layer, because the cross-linked PDMS can not provide the heterogeneous nucleation sites for the growth of MOFs. The $Cu_3(BTC)_2$ crystals showed excellent adhesion with the PDMS matrix. Fig. 2c and d presents a well inter-grown and compacted $Cu_3(BTC)_2$ layer, no pinholes, cracks, or other defects were visible. The diameter of the crystals was in the range of 10-20 μm. The cross-section images revealed that the MOF layer adhered to HFM tightly. Although the PDMS/$Cu_3(BTC)_2$ layer and $Cu_3(BTC)_2$ layer couldn't be distinguished clearly in Figure 2, the silicon of the EDS spectra presented the existence of the PDMS/$Cu_3(BTC)_2$ layer (Fig. S5 ESI†). In addition, the dense layer of the PSf HFM changed to a macropores structure after crystallization (Fig. 2b and d), which may be beneficial for the high gas permeance.

For comparison, we also tried to grow a continuous $Cu_3(BTC)_2$ layer on PSf HFM directly, but those attempts were failed. The SEM images showed that $Cu_3(BTC)_2$ crystals were uncontinuous (Fig. S6 ESI†). The MOF crystals were easier to grow in the solution than on the HFM, which demonstrated that the PDMS/$Cu_3(BTC)_2$ layer was important in the formation of a defect-free $Cu_3(BTC)_2$ membrane.

To examine the reproducibility of trinity membrane, two additional membranes were synthesized. The SEM images showed that a well inter-growth and compact $Cu_3(BTC)_2$ layer was appended on the PSf HFM (Fig. S7 ESI†). This indicates that a good reproducibility of the membranes can be obtained by taking our synthesis procedures.

By utilizing our method, we can further successfully synthesize other MOF layer on different substrates, such as grew $Cu_3(BTC)_2$ or ZIF-8 layer on various polymer hollow fiber membranes, ceramic membrane, and even grew the ZIF-8 layer on filter paper (Fig. S8 ESI†).

Tab. 1 The permeation properties and ideal separation factor of different membranes at room temperature.

membrane	Permeance 10^{-8} mol/(m^2·s·Pa)		ISF
	H_2	CO_2	
M1	188.1	21.2	8.85
M2	48.5	2.3	21.03

M1-PSf HFM with PDMS/$Cu_3(BTC)_2$, M2-trinity membrane.

To further assess the integrity of the prepared membranes, different membranes of PSf HFM with PDMS/$Cu_3(BTC)_2$ (M1) and trinity membrane (M2) were evaluated in gas permeation tests. The permeation results of H_2 and CO_2 through different membranes at 25°C and 1 bar are shown in **Tab. 1**. The M1 had high H_2 permeance of 1.88×10^{-6} mol/(m^2·s·Pa) (28090 bar), which was about 2 times as that reported for a CAU-1 MMMs.[4a] That can be reasoned to the large blended $Cu_3(BTC)_2$ crystals. They can penetrate through the entire PDMS/$Cu_3(BTC)_2$ layer, thus the gas can go through the $Cu_3(BTC)_2$ crystals easily (Fig. S9 ESI†). The ideal separation factor (ISF) became higher after crystallization and reached about 21.03. The value of M2 was much higher than the Knudsen diffusion coefficient of 4.69 and also larger than the highest value 13.56 for $Cu_3(BTC)_2$ layer membrane reported by Zhou *et al.*[5a]. The results showed that the membrane was suitable for gas separation, and the role of the $Cu_3(BTC)_2$ crystals and $Cu_3(BTC)_2$ layer was important.

The data of N_2 permeance for the trinity membrane were also collected and shown in **Fig. 3**. It's surprising that the N_2

permeance was much greater than CO_2, and the biggest ISF obtained was 7.23. This may be attributed to that the open metal sites of $Cu_3(BTC)_2$ membrane had a very strong adsorption capacity to the polar oxygen of carbon dioxide,[5a, 9] therefore, even the adsorption of carbon dioxide can be increased, but the diffusion rate was much smaller than the other two gases.

Most industrial gas mixtures are multicomponent systems, for example, the kinds of the gases that usually contain the similar kinetic diameter (N_2/CO_2) and the gases controlled by solution–diffusion (H_2/CO_2). Thus for the capture of CO_2 from those systems, the membrane prepared in this study may be an ideal choice.

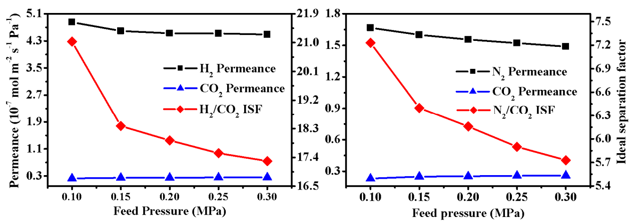

Fig. 3 The gases permeance and ideal selectivity of trinity metal-organic frameworks membrane at different feed pressure.

The stiffness is very important for the application of the MOF layer membranes.[6b] To investigate the mechanical stability of the membrane, the permeation data were also collected under different feed pressures from 1 Bar to 3 Bar. All of the gases permeances decreased slightly. The ISF of H_2/CO_2 and N_2/CO_2 were also reduced, but the values can be obtained in the range of 21.03 to 17.29 and 7.23 to 5.73, respectively (**Fig. 3**). It is shown that the membrane prepared in this study can keep excellent performance under different pressures, which will be helpful for industrial application.

Compared with other literature data for gas separation, the membrane prepared in this study had a excellent separation performance, and also the membrane broke out the Robeson upper bounds easily (see the detail informations in the ESI†, Fig. S10 ESI† and Tab. S1 ESI†).

In summary, reproducible trinity membrane containing membrane substrate, MOFs/PDMS mixture layer and continuous MOFs layer were synthesized. The MOFs particles showed very good adhesion with PDMS and increased the gases permeance dramatically. The well inter-growth MOFs layer was grown on MOFs/PDMS mixture layer successfully when the MOFs in PDMS acted as seeds. The trinity $Cu_3(BTC)_2$ membrane was used for gases permeation tests and exhibited an excellent separation performance. The ISF of the H_2/CO_2 and N_2/CO_2 reached 21.03 and 7.23, respectively. All these results prove that the combining of MMMs and MOFs layers should be an alternative route for preparing MOF membranes with high performance conveniently.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, FTIR, SEM, and comment on gas permeation of the membrane. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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The table of contents: Mixed-matrix membrane and MOF layer were integrated to synthesize novel trinity MOF membranes with excellent performance by using different substrates.

Title: Synthesis of trinity metal-organic framework membranes used for CO_2 capture