Room-temperature in situ synthesis of MOF@MXene membrane for efficient hydrogen purification

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A B S T R A C T

MXene-based membranes with well-defined nanochannels are promising for gas separation. However, manipulating the interlayer structure to obtain high permeance and selectivity remains a great challenge. Herein, we report the construction of MOF@MXene membrane with significantly enhanced gas permeance and selectivity using room-temperature in situ synthesized MOF-801@MXene nanosheets as building blocks. Specifically, negatively charged MXene nanosheets can anchor Zr-metal ions from the surrounding through electrostatic interaction, and then coordinate with ligands at room temperature, yielding MOF-801 crystals with a particle size of approximately 20 nm uniformly grown on the MXene nanosheets. The membranes were then fabricated by vacuum filtration of the as-synthesized MOF-801@MXene nanosheets on the surface of porous organic substrate. The physicochemical properties of the as-synthesized MOF-801@MXene nanosheets and corresponding membranes were observed by XPS, AFM, SEM, IR, XRD, and gas adsorption analysis. Because the MOF-801 crystals can provide more transport channels for H₂ molecules and exhibit high adsorption capacity for CO₂ molecules to impede its diffusion, the resulting membranes display excellent gas separation performance with a H₂ permeance of 2200 GPU and H₂/CO₂ selectivity of 26.6. Such a facile preparation method for MOF@MXene membranes could provide valuable insights into the development of advanced materials for molecular separation.

1. Introduction

Membrane-based separation technology with low energy consumption and easy operation has piqued significant interest in gas separation research [1,2]. At the core of membrane separation are materials, which are dominated by polymers. However, the polymer membranes generally suffer from a trade-off relationship between permeability and selectivity [3]. In the past decade, two-dimensional (2D) materials with extraordinary permeation properties have been demonstrated as promising building blocks for constructing laminar membranes for molecular separation [4–9]. With thickness down to the atomic scale, 2D materials can minimize transport resistance to achieve a high-throughput separation, overcoming the trade-off limit [10].

A recent and important family of 2D materials, MXene, has recently attracted increasing attention because of its unique physicochemical properties. Its chemical formula is $M_{n-1}A_xT_x$ (n = 1, 2, 3), where M represents an early transition metal, X is carbon or nitrogen and Tₓ refers to the terminated groups including H, O and F generated from the synthesis in aqueous medium [11,12]. Tₓ can create open narrow nanochannels within stacked MXene laminates for selective molecular transport. Generally, ultrathin MXene nanosheets are synthesized by chemical etching of the “A” element from its precursor MAX powders (where A is a group IIIA or IVA element), followed by sonication and centrifugation [13–16]. Due to the unique characteristics of atomic thickness, micrometer lateral size and hydrophilic nature, MXene nanosheets are widely assembled as molecular-sieving membranes [17–25].

Compared with other 2D materials, such as graphene oxide (GO), MXene membranes with robust channels can maintain structural integrity even after being immersed in an aqueous solution for more than one month [18], whereas GO membranes tend to disintegrate in water owing to strong hydration between GO nanosheets and water molecules [26,27]. In addition, note that the essential difference between them lies in the structural diversity of MXene based on various transition metals (e.g., Ti, Cr, V), enabling MXene nanosheets with versatile regulated physicochemical properties for various applications [11,28]. More interestingly, MXene probably can be employed as a metal source for the synthesis of metal–organic frameworks (MOFs), further boosting the research on the 2D or 3D membranes for molecular separation [29,30].

Until now, the most studied MXene is Ti₃C₂Tx, which has been widely prepared as a separation membrane for water purification [31–34]. Nevertheless, there are very few studies on MXene membranes for gas separation. Wang et al. first reported the construction of a
laminar MXene membrane with aligned and regular channels for high performance separation of H\(_2\)/CO\(_2\), which opened a path to employ MXene-based membranes for gas separation [35]. Very recently, our group designed a type of tunable MXene film with thickness down to 20 nm [36]. Then, its stacking behavior and interlayer spacing were precisely manipulated by functionalizing borate and PEI molecules, achieving the transformation from H\(_2\)-selective channels to CO\(_2\)-selective channels. Xu and co-workers fabricated self-crosslinked MXene hollow fiber membranes using a facile thermal treatment process [37]. The as-synthesized membranes with effective interlayer space adjustment demonstrated excellent H\(_2\)/CO\(_2\) gas separation performance with good operational stability. However, these studies have focused on manipulating interlayer space via cross-linking strategies or utilizing intrinsic nanochannels within MXene membrane, whereas introducing porous materials such as MOFs into MXene membranes to improve molecular separation efficiency has not yet been thoroughly investigated. The conventional intercalation method is physical blending [38–40], where porous crystals need to be first synthesized and then mixed with membrane building blocks, which is complex and time-consuming. Novel approaches for inserting MOF crystals into MXene membranes are required.

In this study, we report the in situ synthesis of MOF-801@MXene materials at room temperature as building blocks for assembling a laminar membrane for H\(_2\)/CO\(_2\) separation (Fig. 1). Specifically, in the designed system, the negatively charged MXene nanosheets can anchor Zr\(^{4+}\) from the surrounding solution through electrostatic interactions and then coordinate with ligands to yield MOF-801 crystals uniformly distributed on the nanosheets. Then, the as-synthesized MOF-801@MXene nanosheets were stacked as laminar membranes by vacuum filtration. The MOF-801 material has a network of porous tetrahedral and octahedral cages, which are interconnected by a triangular window-the entrance to sieve molecules. The facile intercalation of MOF-801 crystals is expected to enlarge the nanochannels and provide additional molecular sieving channels for H\(_2\)/CO\(_2\) separation, significantly improving H\(_2\) permeance and H\(_2\)/CO\(_2\) selectivity.

2. Experimental

2.1. Materials

Ti\(_3\)AlC\(_2\) MAX powders were provided by 11 technology Co., Ltd, China. Lithium fluoride (LiF, 99.9%) and Zirconium oxychloride octahydrate (ZrOCl\(_2\)-8H\(_2\)O, 98%) powders were obtained from Sigma-Aldrich. Fumaric acid (C\(_4\)H\(_4\)O\(_4\), 99%) was provided by Alfa Aesar. HCl (36%–38%), acetic acid (C\(_2\)H\(_4\)O\(_2\), ≥99.5%) and ethanol (≥99.7%) were obtained from Sinopharm. The porous substrates poly tetra fluoroethylene (PTFE) with pore size of 50 nm were obtained from Shandong Meagvision. Deionized water was used in the all experiments.

2.2. Synthesis of Ti\(_3\)C\(_2\)T\(_x\) MXene nanosheets

The Ti\(_3\)C\(_2\)T\(_x\) MXene nanosheets were synthesized as in our previous papers [8,41,42]. 0.67 g LiF powder was dissolved in 10 mL of an HCl solution (6 M). After stirring for ~40 min, 1 g Ti\(_3\)AlC\(_2\) was added to the above mixture with stirring at 35 °C for one day. The resulting product was washed using water and ethanol several times via centrifugation until the pH of the supernatant was ~7. The sediment was dispersed in water via sonication under the nitrogen atmosphere for 1 h to delaminate the MXene powders. Then, un-exfoliated MXene powders were removed via centrifugation at 3500 r.p.m. for another 1 h. Finally, the concentration of the obtained MXene solution was ~0.2 mg mL\(^{-1}\).

2.3. Synthesis of MOF-801 crystals

MOF-801 particles were obtained according to a previous report with modifications [43]. Fumaric acid (87 mg, 0.75 mmol) and ZrOCl\(_2\)-8H\(_2\)O (242 mg, 0.75 mmol) were dissolved in a 10 mL aqueous solution with a specific volume of acetic acid, which was heated at 60 °C for 12 h. The resulting colorless crystals were collected and washed several times with 100 mL of water. Finally, the solid was dried at 80 °C in vacuum for 12 h.

2.4. In situ synthesis of MXene@MOF-801 nanosheets

The MXene@MOF-801 nanosheets were in situ synthesized using a one-step method at room temperature. In detail, fumaric acid (0.0375 or 0.05 or 0.075 or 0.15 mmol), equimolar ZrOCl\(_2\) and a specific amount of MXene nanosheets were dispersed into a 100 mL aqueous solution with acetic acid in a 250-mL Teflon beaker, and then the mixture was held at room temperature with magnetic stirring for 1 h to form a homogeneous solution for membrane fabrication.

![Fig. 1. Illustration of in situ synthesis of MXene@MOF-801 nanosheets at room temperature.](image-url)
2.5. Membrane fabrication

A facile vacuum filtration method (Fig. S1) was applied to prepare MXene-based membranes. The as-synthesized MXene@MOF-801 nanosheets were deposited on the surface of a porous PTFE substrate to form a separation layer driven by a pressure of 1 bar, and then dried at 30 °C under vacuum for 12 h.

2.6. Characterization

The morphology of the materials was studied by the field emission scanning electron microscopy (FESEM, JSM-7600 F, Japan), Atomic Force Microscope (AFM, XE-100, Park SYSTEMS, Korea) and Transmission electron microscopy (TEM, JEM-2100 F, Japan Electron Optics Laboratory Co., LTD, Japan). The crystal phases of powders and membranes were measured by X-ray diffraction (XRD) (Rigaku, MiniFlex 600, Japan). X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250, USA) and Fourier Transform Infrared Spectrometer (FTIR, AVATAR-FT-IR-360, Thermo Nicolet, USA) were applied to study the chemical property of resulting membranes. Zeta potential analysis (Zetasizer Nano ZS90, Malvern, UK) is carried to characterize the solutions. The hydrophilicity of materials was studied by contact angle (DSA100, Kruss) drop-meter. The mechanical property of membranes was determined using a universal testing machine (CMT-6203, Meister Industrial Systems Co., LTD, China).

2.7. Gas separation performance measurement

The gas permeation measurements were conducted by a home-made apparatus. The gas transport behavior was evaluated by constant pressure/volume method [44]. The single gas permeance was detected via a bubble flow meter, which was carried out at 1 bar and 25 °C. When the system reached a steady state, the test was repeated for at least three times. The gas permeability was calculated using the following equation:

\[
P = \frac{1}{\Delta p} \left( \frac{V}{A} \right) \frac{dV}{dt} = \frac{P_{\text{mem}}}{76} \left( \frac{dV}{dt} \right)
\]

(1)

where \( P \) is the gas permeance (1 GPU = 10^{-6} \text{ cm}^3 \text{ (STP)} \text{ cm}^{-2} \text{s}^{-1} \text{ cmHg}), \( \Delta p \) represents the transmembrane pressure (atm), \( P_{\text{mem}} \) stands for the atmospheric pressure (atm), \( T \) is the permeate temperature (°C), \( A \) is effective membrane area (m²), and \( dV/dt \) stands for the volumetric displacement rate in the bubble flow meter.

The ideal selectivity \( \alpha \) can be calculated using the following equation

\[
\alpha = \frac{P_A}{P_B}
\]

(2)

where \( P_A \) and \( P_B \) are the permeabilities of pure gases A and B, respectively.

Mixed-gas test, H₂/CO₂ (50/50, V/V) was used as feed gas, with a total flux of 30 mL min⁻¹, while Argon was chosen as sweep gas with a flux of 30 mL min⁻¹. The selectivity for binary gas mixture could be obtained by the following equation:

\[
\alpha_{A,B} = \frac{Y_A}{X_A} \cdot \frac{X_B}{Y_B}
\]

(3)

where \( X \) and \( Y \) are the volumetric fractions of the one component in the feed and permeate, respectively.

3. Results and discussion

3.1. Synthesis and characterization of MXene nanosheets

\( \text{Ti}_2\text{C}_2\text{T}_x \) MXene nanosheets were synthesized by etching the aluminum (Al) layer of the bulk MAX precursor using a widely adapted wet etching method (Fig. 2a). Instead of a hazardous etchant, such as hydrofluoric acid (HF), we selected a mixture of HCl and LiF as the etchant. As shown in SEM images in Fig. 2b and c, after etching the Al atoms of the MAX precursor, the obtained MXene powder exhibit an accordion-like structure, indicating successful etching. This was confirmed by XRD results, which showed the generation of new characteristic peaks at ~7° (Fig. 2e). Notably, the diffraction peaks corresponding to the MAX precursor still appeared, while they could easily be removed by the following ultrasonication and centrifugation. Ultrathin MXene nanosheets can be easily obtained by the sonication of the resulting MXene powders. The SEM and TEM images revealed that etched MXene nanosheets with lateral sizes of 12 µm were thin and nearly transparent without structural defects (Fig. 2d and f). Moreover, the MXene nanosheets with excellent hydrophilicity could disperse in water evenly (Fig. S2), exhibiting the Tyndall scattering effect (insert in Fig. 2d). In addition, the resulting MXene nanosheets exhibited a uniform thickness of 12 nm, indicating that one or two layers of the MXene nanosheets were successfully obtained (Fig. 2g). These as-synthesized MXene nanosheets are favorable for assembling 2D membranes (Fig. S3) with abundant in-plane nanogap and transport channels for precise gas separation.

3.2. Synthesis and characterization of MOF-801@MXene nanosheets

MOF crystals with regular and highly tunable pore structures are chosen to create nanochannels of 2D membranes to facilitate molecular transport [45–47]. Here, we investigated a water-stable MOF material, MOF-801, which can be obtained from a green synthesis approach with water as the solvent at low temperatures [43,48]. Therefore, we employed a facile one-step method for in situ growth of MOF-801 on MXene nanosheets by stirring a mixture containing the nanosheets, metal source (ZrOCl₂) and ligand (fumaric acid) at room temperature. As shown in Fig. 3a, the zeta potential of the MXene dispersion was approximately 33.2 mV, indicating that the nanosheets were negatively charged and that the Zr-metal source was positively charged. Thus, during the room temperature reaction, positive Zr⁴⁺ could first attach to the surface of negatively charged MXene nanosheets by electrostatic interactions (Fig. 3a), and then coordinate with the ligand (fumaric acid), in situ generating MOF-801 crystals on the surface of the MXene nanosheets. In addition, after mixing MXene and the metal source with an increased weight ratio, the zeta potential of the solution became approximately zero, demonstrating that the negatively charged groups on the MXene nanosheets were gradually paired with metal cations and no excess metal ions existed in the solution, which enabled MOF crystals in situ grown on the nanosheets instead of in the solution. It is worth noting that when the metal ions are excessive, the zeta potential of the mixed solution is positively charged, indicating that there are residual metal ions in the solution to generate MOF crystals, which may damage the laminar membrane structure. Most importantly, it is difficult to observe the aggregation of the nanosheets in the mixed solution after stirring and standing for 1 h alternately (Fig. S4), which benefits the preparation of a uniform membrane. Fig. 3b presents the AFM image of the resulting MOF-801@MXene nanosheets. The results show that the nanosheets exhibit a sheet-like structure with a thickness of ~20 nm, indicating the successful growth of MOF-801 crystals. In addition, we characterized the nanosheets by TEM. Although we could observe dark spots with small sizes uniformly dispersed on the nanosheet surface (Fig. 3c and d), which represent MOF-801 crystals verified by EDX mapping (Fig. 3d), the signal is weak, probably because MOF materials show no resistance to electron beam irradiation [6]. Nevertheless, the diffraction peaks of the MOF-801@MXene nanosheets agree well with those of simulated MOF-801 over the 20 range of 8°–10°. These results further demonstrate the successful generation of MOF-801 crystals on MXene nanosheets using a room-temperature in situ synthesis method. As a result, the synthesized MOF-801@MXene nanosheets can serve as
Fig. 2. (a) Fabrication process of MXene nanosheets from their precursor MAX powders; SEM images of (b) bulk MAX precursor and (c) MXene powders, and inserts are the corresponding digital images of the powders; (d) SEM images of the resulting MXene nanosheets, and the insert is the Tyndall scattering effect in MXene suspension in water; (e) XRD patterns of MAX and MXene powders; TEM (f) and AFM (g) images of MXene nanosheets, and the inserts in (g) are the corresponding height profiles of MXene nanosheets.

Fig. 3. (a) Zeta potential for MXene, ZrOCl₂ and MXene-ZrOCl₂ solutions; the concentrations are 0.01, 0.16, 0.11, 0.17 and 0.49 mg/mL, respectively; (b) AFM image, (c) STEM HAADF image, (d) EDX mapping and (e) XRD patterns of MOF-801@MXene nanosheets.
building blocks to assemble laminar membranes for efficient molecular separation. The crystals existing in the layers of the composite membrane are expected to improve separation efficiency by increasing the interlayer distance.

### 3.3. Physicochemical properties of membranes

The resulting nanosheets were deposited on the surface of the porous substrate (Fig. S5) to assemble laminar membranes using a facile vacuum filtration method. As shown in Fig. 4a, the as-synthesized dark black MOF-801@MXene membrane exhibited a flat surface morphology with fewer wrinkles than that of the MXene membranes (Fig. S6a). Meanwhile, the average surface roughness of the MOF-801@MXene membrane is ~62.2 nm, which is significantly larger than that of the MXene nanosheets (29.6 nm) (Fig. 4b, Fig. S6c and Fig. S7) owing to the intercalation of MOF crystals between the MXene nanosheets. In addition, the cross-section SEM image in Fig. 4c shows an undestroyed laminate layer with larger thickness owing to the regular presence of MOF-801 crystals between the layers (Fig. S6). The EDS mapping results show that a new Zr element was observed on the MOF-801@MXene membrane and the elements Ti, C, and O are uniformly distributed (Fig. 4d and e, Figs. S6d and S8-S9), suggesting the successful formation of MOF-801 crystals uniformly distributed on the surface of the MXene nanosheets.

We also investigated the mechanical properties of the membranes by tensile testing. As shown in Fig. S10, the critical tensile load of the MOF-801@MXene composite membrane (32.4 N) was slightly lower than that of the pristine MXene membranes (37.0 N). The intercalation of MOF crystals increased the brittleness of the composite membranes, leading to a lower elongation (22.3% vs 33.3%). Nonetheless, the composite membranes can still maintain the intrinsic laminar structure to facilitate control the amount of MOF crystals (Fig. 4). When the amounts of crystals were excessive, the membrane became very brittle, leading to the structural collapse. Furthermore, we investigated the chemical properties of the membranes by FTIR. As shown in Fig. 5a, in the FTIR spectrum of MOF-801@MXene membrane, the peaks at ~1724, ~1652.7 and ~1524 cm⁻¹ are recognized as the –C=O–O bond, and the peaks at ~1068 and ~661 cm⁻¹ refer to the -C=O and Zr–O bonds, which are generated from the functional groups of the fumaric acid and metal cluster in MOF-801 [49]. More information about the chemical structure and element composition can be observed by XPS. It can be seen from Fig. 5b that the Zr element was detected for MOF-801@MXene compared with the pristine MXene nanosheets. Besides, the Zr 3d spectrum of MOF-801@MXene shown in Fig. 5c displays the binding energies of Zr 3d₃/₂ and Zr 3d₅/₂ states, which are located at 185.1 and 182.8 eV, respectively [50]. Furthermore, from the Cls spectrum of MOF-801@MXene, the intensities of O–C=O and C–C were enhanced compared with that of MXene, evidencing the presence of MOF-801 crystals on the surface of the MXene nanosheets.

### 3.4. Gas separation performance

#### 3.4.1. Effects of MXene nanosheets loading

The gas permeation behavior of the membranes was investigated. First, we investigated the effect of nanosheets loading on pristine MXene membranes for H₂/CO₂ separation. Adjusting MXene nanosheets deposition could facilely achieve the precise manipulation of MXene layer thickness (Fig. S11). As shown in Fig. 6, H₂ permeance decreased, whereas the H₂/CO₂ selectivity increased with an increase in membrane loading from 0.03 to 0.14 mg/cm². The MXene membrane with a loading of 0.03 mg/cm² exhibits high H₂ permeance of ~2637 GPU, whereas H₂/CO₂ selectivity is only ~4, probably due to the existence of many non-selective defects. Upon increasing the nanosheets loading to greater than 0.08 mg/cm², the selectivity increases to ~17, and then almost remains stable, which far exceeds the selectivity of the Knudsen diffusion of 4.7 [9], demonstrating that defects have been gradually eliminated with increasing MXene layer thickness. The MXene membrane with nanosheets deposition of 0.08 mg/cm² exhibited the highest separation performance with H₂ permeance of ~773 GPU and selectivity of ~17. Therefore, 0.08 mg/cm² was chosen as the optimized MXene nanosheets deposition for developing the MOF-801@MXene membrane.

#### 3.4.2. Effects of MOF reactant concentration

We further observed the effects of the amounts of reactants on the gas transport properties of the MOF-801@MXene membranes. Fig. 7 shows that the pristine MXene membranes exhibit a low H₂ permeance of ~773
GPU and H$_2$/CO$_2$ selectivity of ~17. However, after introducing MOF-801 crystals, H$_2$ permeance is improved to above 1000 GPU and the selectivity is enhanced to ~30. We speculate that the uniformly grown MOF-801 crystals on the MXene nanosheets not only enlarge the transport channels within the membranes, but also offer additional molecular-sieving channels endowed by the intrinsic pore structure of MOF-801, leading to fast and efficient sieving of H$_2$ over CO$_2$. In addition, notably, as shown in Fig. S12, when the amounts of reactants were excessive, isolated MOF nanocrystals tended to be generated in the bulk solution, significantly increasing the brittleness of the composite membrane, which could destroy the initial structure to sacrifice the molecular sieving ability. Hence, the MOF-801@MXene membranes with an optimized amounts of reactants of 0.05 mmol exhibited high H$_2$/CO$_2$ selectivity of up to 29.4 and H$_2$ permeance of 2334 GPU.

To highlight the potential advantages of our MOF-801@MXene membrane by the room-temperature in situ synthesis approach, we also employed the well-known physical intercalation strategy to fabricate a MOF-801-intercalated MXene membrane (labeled as MOF-801-MXene), which was generated from mixing pre-synthesized MOF-801 crystals with MXene dispersion as the filtration solution. We first synthesized the MOF-801 crystals according to the low-temperature hydrothermal method [43]. The crystals with a spherical structure have a uniform size distribution with an average particle size of ~20 nm (Fig. 8a and Fig. S13). Meanwhile, the XRD patterns of the crystals were also consistent with the simulated one, indicating the high phase purity.
of the synthesized MOF-801 nanocrystal (Fig. 8b). Then we introduced the crystals into MXene membranes by physical blending and evaluated the gas transport behavior (Note: the mass fraction of MOF is ~13.7%, which is equal to that of the optimized MOF-801@MXene membrane calculated from the XPS results.). As shown in Fig. 8d, the H<sub>2</sub> permeance of MOF-801-MXene membrane is improved to ~1824 GPU, approximately 2.5 times greater than that of the pristine MXene membrane. However, the H<sub>2</sub>/CO<sub>2</sub> selectivity is dramatically reduced to ~5.1. This may be attributed to the isolated MOF crystals dispersed in the solution changing the stacking behavior of the nanosheets, leading to local agglomeration of crystals within membranes, as confirmed by the real morphology of membranes shown in Fig. 8c and Fig. S14. In contrast, the MOF-801@MXene membrane exhibits enhanced H<sub>2</sub> permeance of 2334 GPU and selectivity of 29.4, which are significantly superior to those of the pristine MXene and MOF-801-MXene membranes, and may be attributed to the uniform distribution of MOF-801 crystals on the MXene nanosheets (confirmed by AFM and TEM results, Fig. 3) to enlarge the laminar transport channels and endow the intrinsic MOF structure with abundant additional sieving channels.

Fig. 8. (a) TEM images and (b) XRD patterns of MOF-801 crystals; (c) SEM surface image of MOF-801-MXene membrane generated from the physical mixing of nanosheets and crystals; (d) Pure gas separation performance for H<sub>2</sub>/CO<sub>2</sub> of pristine MXene, MOF-801-MXene and MOF-801@MXene membranes, which was measured at 25 °C and 1 bar.

3.4.3. Effects of operation conditions and performance comparison

The effect of feed pressure on H<sub>2</sub>/CO<sub>2</sub> separation has also been investigated. As shown in Fig. S15, H<sub>2</sub>/CO<sub>2</sub> separation performance decreased with feed pressure, probably due to the interlayer (out-of-plane) and in-plane slit like pores sizes changed under high pressure [36]. To study the structural stability of the MOF-801@MXene membrane, continuous separation of mixed gas (50:50H<sub>2</sub>/CO<sub>2</sub>, volume percent) was tested. Fig. 9a shows that the MOF-801@MXene membrane maintain excellent separation performance with permeance of ~2200 GPU and selectivity of ~26 during a 120-h long-term operation test, indicating excellent mechanical stability even under long-term continuous permeation tests, which is important for real world applications. Meanwhile, note that the mixed gas separation performance is slightly lower than that of single gas permeation, probably due to the competitive diffusion or adsorption of H<sub>2</sub> and CO<sub>2</sub> [35, 44]. The separation efficiency far exceeds the 2008 Robeson upper bound for H<sub>2</sub>/CO<sub>2</sub> separation of polymeric membranes [51], and remains highly competitive compared with that of various previously reported membranes (Fig. 9b and Table S1). This promising separation performance is attributed to the facile introduction of MOF-801 crystals uniformly

Fig. 9. (a) Long-term separation of equimolar H<sub>2</sub>/CO<sub>2</sub> (50:50H<sub>2</sub>/CO<sub>2</sub>, volume percent) through MOF-801@MXene membrane at 25 °C and 1 bar; (b) Comparison of H<sub>2</sub>/CO<sub>2</sub> separation performance of MOF-801@MXene membrane, and information about the data points is given in Supplementary Table 1.
distributed within MXene nanosheets.

3.5. Transport mechanisms analysis

To further understand the role of MOF crystals within MXene membranes for gas separation, we conducted a series of experiments. We first observed the interlayer spacing of membranes. As shown in Fig. 10a, the pristine MXene membrane shows a diffraction peak at 20 of 6.72°, corresponding to a d-spacing of 1.31 nm, which is calculated based on the Bragg’s law [35]. After the room temperature in situ growth of MOF-801 crystals on MXene nanosheets, the characteristic peak slightly shifts to lower 2θ values, representing a d-spacing of 1.35 nm. Considering that the thickness of single MXene nanosheets is ~0.98 nm [52], the interlayer empty height of composite membranes with MOF nanocrystals between the layers increased to 0.37 nm from 0.33 nm, demonstrating that intercalated MOF-801 crystals efficiently enlarge the transport channels within MXene membranes, as illustrated in Fig. 10c. It is worth noting that interlayer spacing of the composite membrane changes very weakly after introducing MOF crystals with a size of ~20 nm, probably due to the excellent flexibility of MXene nanosheets with a micrometer lateral size can render a portion of the interlayer channels to a sub-nanometer level [53]. Meanwhile, the MOF-801 crystals (Fig. S16) present a face-centered cubic (fccu) topology with interconnected tetrahedral (green ball) and octahedral (orange ball) cages (the diameters are ~5.2 and 7.4 Å, respectively) whose faces comprise a triangular window with aperture size of 4.7 Å—the sole entrance to the MOF pore system for molecular sieving [48,54], providing additional molecules transport channels (Fig. 10c). During the permeation process of H₂ or CO₂ molecules through the MOF-801@MXene membrane, H₂ with a smaller molecular kinetic diameter k_d (2.89 Å) than of CO₂ (kinetic diameter, k_d: 3.3 Å) would encounter less transport resistance, thereby significantly improving H₂ permeance of the MOF-801@MXene membrane. Meanwhile, the introduction of MOF-801 crystals would inevitably increase the tortuosity of the diffusion path. Larger CO₂ molecules would encounter more resistance and would move more slowly through membranes. Besides, the MOF-801 crystals possess exhibited higher adsorption ability toward CO₂ molecules than H₂ molecules (Fig. 10b), which could inhibit the permeation of CO₂ through the membrane, significantly enhancing H₂/CO₂ selectivity. These results also confirm our above-mentioned speculation that MOF-801 crystals enlarge laminar transport channels and provide additional molecular sieving channels simultaneously, contributing to the enhancement of H₂ permeance and H₂/CO₂ selectivity.

4. Conclusions

In summary, we have demonstrated the construction of a novel 2D MXene membrane through a facile room-temperature in situ synthesis approach. The uniform intercalation of porous MOF crystals on MXene nanosheets enlarges the laminar transport channels between the nanosheets and simultaneously provides extra molecular sieving channels. As a result, the as-synthesized MOF-801@MXene membrane exhibits significantly enhanced gas permeance and selectivity for H₂/CO₂ separation (H₂ permeance: 2200 GPU, H₂/CO₂ selectivity: 26.6), which transcends the upper bound of state-of-the-art membranes. The facile synthesized MOF@MXene membrane contributes to the development of 2D material membranes for gas separation. Moreover, it can provide a platform for the topological synthesis and fabrication of MOF-MXene heterostructure membranes enabled by 2D MXene precursors.

Credit authorship contribution statement


Fig. 10. (a) XRD patterns of pristine MXene and MOF-801@MXene membranes; (b) Gas adsorption of pristine MXene, MOF-801 and MOF-801@MXene at 25 °C; (c) the roles of MOF-801 crystals in molecule transport.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2022.121097.

References