Abstract: Preferred-orientation control has significant impact on the separation performance of MOF membranes. Under most conditions the preferred orientation of MOF membranes is dominated by the Van der Drift mechanism of evolutionary growth selection so that the obtained orientation may not be optimized for practical application. In this study, highly c-oriented NH$_2$-MIL-125 membranes were prepared on porous α-alumina substrates by combining oriented seeding and controlled in-plane epitaxial growth. Dynamic air-liquid interface-assisted self-assembly of c-oriented NH$_2$-MIL-125-(Ti) seed monolayers, the use of layered Ti$_3$C$_2$ as the metal precursor, and single-mode microwave heating were crucial in ensuring the preferred c-orientation while simultaneously suppressing undesired twin growth. Owing to reduced grain boundary defects, the prepared c-oriented membranes showed an ideal $H_2/CO_2$ selectivity of 24.8, which was 6.1 times higher than that of their randomly oriented counterparts under similar operating conditions.

In-plane epitaxial growth of highly c-oriented NH$_2$-MIL-125(Ti) membranes with superior H$_2$/CO$_2$ selectivity

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Metal–organic framework (MOF)-based separation membranes have offered unprecedented opportunities for gas separation, such as $H_2$ purification, $CO_2$ capture, and olefin/paraffin separation.[1] Among various factors, preferred-orientation control of MOF membranes has proven to be very effective for improving their separation performance by the ordered arrangement of nanopores, a decrease in grain boundary defects, and reduction in diffusion path lengths.[2] Although diverse methods have been developed for the production of well-intergrown MOF membranes, elaborate control of their preferred orientation has remained a very challenging task.[2a,3] For example, in situ growth methods usually led to the formation of randomly oriented MOF membranes rather than oriented membranes,[4] since in general, nucleation and crystallization of MOF particles occurred simultaneously in the bulk solution and on the substrate surface, thus making precise orientation control particularly challenging except on rare occasions. In contrast, secondary growth enabled more precise control over the preferred orientation of MOF membranes by combining the pre-deposition of oriented MOF seed layers with controlled in-plane epitaxial growth. Nevertheless, in analogy to oriented zeolite membrane synthesis, several technical obstacles still existed in the full utilization of this method: 1) With respect to oriented MOF seed layer deposition, Lai and co-workers preferentially deposited (102) oriented MOF-5 seed layers on α-Al$_2$O$_3$ substrates in situ by a microwave-induced thermal deposition method,[5] and Wang and co-workers successfully attached platelike ZIF-L seeds to substrates along the c-axis through vacuum filtration in the presence of polyethyleneimine.[6] Nevertheless, the facile organization of anisotropic MOF seeds with decent aspect ratios (like coffin-shaped MOF crystals) into highly oriented monolayers on porous substrates has remained a challenging task. 2) With regard to controlled in-plane secondary growth, it has remained a challenging task to suppress undesired twin growth, which may severely impair the separation performance owing to the difficulty in effectively suppressing simultaneous bulk nucleation. 3) High adhesion strength needs to be maintained. As compared with in situ solvothermal growth, the adhesion strength between MOF layers prepared by secondary growth and porous ceramic substrates (such as α-Al$_2$O$_3$) has remained fairly low.[6c,6] Therefore, a new synthetic route was urgently needed to address the above existing issues.

NH$_2$-MIL-125(Ti), one of the most widely studied Ti-MOFs, has emerged as a promising candidate[7] for membrane-based $CO_2$ capture because of its high affinity for $CO_2$, high thermal stability, and straight nanochannels along the c-axis, which were advantageous for the reduction of diffusion paths.[8] Therefore, the fabrication of a highly c-oriented NH$_2$-MIL-125(Ti) membrane was highly desirable owing to the potential for the reduction of diffusion barriers and the elimination of grain boundary defects.

Being analogous to MOFs, in recent decades significant progress was also made in the fabrication of oriented zeolite membranes (in particular b-oriented MFI zeolite membranes). For example, we developed a general route for the synthesis of highly b-oriented MFI films/membranes.[9] First, a facile air–liquid interface-assisted self-assembly (ALIAS)
method was developed to deposit highly b-oriented MFI monolayers on porous substrates, relying on geometric factors and the intrinsic hydrophobicity of anisotropic MFI microcrystals.\cite{9a,b} Second, a microwave-assisted hydrothermal method was employed to maintain the desired in-plane epitaxial growth while simultaneously suppressing undesired twin growth, relying on the unique nucleation-related bottleneck effect of microwave irradiation.\cite{9c} Considering the similarity between MOFs and zeolites, it is expected that our experience could provide insight into the fabrication of well-intergrown and highly c-oriented NH$_2$-MIL-125(Ti) membranes.

In general, two modes of microwave heating exist, that is, single-mode and multi-mode.\cite{10} In a single-mode reactor, the microwave field is generated by a single magnetron and guided by a rectangular waveguide to the reactor. The microwave interacts with the precursor solution through a relatively homogeneous electromagnetic field; moreover, the single-mode configuration demands a small cavity, thus yielding a high-density microwave field. In contrast, a multi-mode microwave reactor generally has a much larger cavity so that the energy density is considerably lower; moreover, the microwave field, which is generated by one or more magnetrons, is randomly distributed in the cavity, thus leading to a heterogeneous heating profile. Multi-mode microwave heating has been widely applied in the hydrothermal/solvothermal synthesis of molecular sieve membranes. Potential applications of single-mode microwave heating, however, have rarely been explored in this field. Considering that single-mode microwave heating is advantageous over its multi-mode counterpart in terms of microwave field uniformity and intensity, it is expected that enhanced nonthermal effects and higher absorption efficiency can be achieved, which may potentially lead to improved microstructure when single-mode microwave heating is applied in the synthesis of molecular sieve membranes.

In the present study, we developed a novel route for the preparation of highly c-oriented NH$_2$-MIL-125(Ti) membranes on porous α-Al$_2$O$_3$ substrates (shown in the Experimental Section and the Supporting Information). Among various factors, the use of turbulent DI water layers as temporary soft substrates during the oriented seeding process, layered TiS$_x$ as titanium precursors, and a single-mode microwave reactor during the in-plane epitaxial growth process was found to be essential for producing the desired microstructure (Figure 1).

NH$_2$-MIL-125(Ti) seeds were synthesized by a simple solvothermal method.\cite{9b} Prepared NH$_2$-MIL-125(Ti) seeds were highly uniform (ca. 800 nm in length and ca. 200 nm in thickness) and exhibited circular plate morphology (see SI-2 in the Supporting Information). Prior to oriented deposition, NH$_2$-MIL-125(Ti) seeds were stirred continuously in ethanol until uniformly dispersed.

The first step involved the oriented deposition of a NH$_2$-MIL-125(Ti) monolayer (see SI-3). Before deposition, a rectangular container was filled with DI water. The NH$_2$-MIL-125(Ti)-containing ethanol solution was slowly injected at the turbulent air–liquid interface with a microsyringe until the final formation of a closely packed and highly c-oriented NH$_2$-MIL-125(Ti) monolayer, which could be readily transferred to the porous α-Al$_2$O$_3$ substrate. SEM results indicated that the prepared NH$_2$-MIL-125(Ti) monolayer was uniform and closely packed (Figure 2a). Moreover, it was observed that almost all NH$_2$-MIL-125(Ti) seeds were anchored to the substrate with their largest facets and in close contact with each other. XRD patterns further confirmed the dominance of a preferred c-orientation, since only (00l) diffraction peaks survived in the XRD pattern (Figure 3b). In contrast to MFI-type zeolites,\cite{9d} in this study it was vital to maintain the air–liquid interface in a turbulent state with a circulating water pump to promote the organization of NH$_2$-MIL-125(Ti) seeds into a closely packed and c-oriented monolayer; otherwise, NH$_2$-MIL-125(Ti) seeds would be loosely distributed on the substrate, which could be attributed to insufficient driving force for the successful self-assembly of NH$_2$-MIL-125(Ti) seeds (see SI-4).

Besides ethanol, various other solvents, including methanol, n-/i-propanol, n-butanol, acetone, and dichloromethane,
Our recent study showed that solid layered titanium disulfide (TiS₂) could serve as an efficient metal source for the synthesis of NH₂-MIL-125(Ti) powders\[10\]. As compared with the commonly used TPOT reagent, layered TiS₂ dissolved in the precursor solution more slowly and homogeneously under solvothermal conditions, which was potentially advantageous for the suppression of undesired twin growth. Furthermore, relying on the unique nucleation-related bottleneck effect of microwave irradiation\[9c,15\] layered TiS₂ was used in this study as the metal source, and single-mode microwave heating was employed for more effective suppression of bulk nucleation during the epitaxial growth of NH₂-MIL-125(Ti) membranes. SEM images indicated that after secondary growth, well-intergrown NH₂-MIL-125(Ti) membranes with few twin crystals had formed on porous α-Al₂O₃ substrates (Figure 2d). A cross-sectional image further indicated that prepared NH₂-MIL-125(Ti) membranes were approximately 0.5 µm thick (Figure 2d). The EDXS pattern of the cross-section further showed that there existed a sharp boundary between the NH₂-MIL-125(Ti) top layer and the porous α-Al₂O₃ substrate (see SI-9), thus indicating that the NH₂-MIL-125(Ti) layer did not penetrate into the substrate. The XRD pattern (Figure 3c) of prepared NH₂-MIL-125(Ti) membrane further showed strong (002) and (004) reflections at 2θ values of 10.3 and 20.6°, respectively, which unambiguously demonstrated that the NH₂-MIL-125(Ti) layer was indeed predominantly c-oriented. Furthermore, there was a very weak diffraction peak located at a 2θ value of 6.7°, which was assigned to the (101) crystal plane of the NH₂-MIL-125(Ti) phase, as shown in Figure 3c. The low intensity of other diffraction peaks clearly indicated that twin crystals were rare.

The simultaneous use of layered TiS₂ as the metal source and single-mode microwave heating was indispensable to maintain the desired in-plane epitaxial growth; otherwise, the undesired twin growth could not be effectively suppressed (see SI-10). Moreover, only by single-mode microwave heating could well-intergrown NH₂-MIL-125(Ti) membranes be obtained. In contrast, the size of NH₂-MIL-125(Ti) seeds only slightly increased and substantial intercrystal defects existed in the case of multi-mode microwave heating (see SI-11). To the best of our knowledge, the single-mode microwave-assisted hydrothermal/solvothermal synthesis of molecular sieve membranes has not been reported previously. The superior microstructure of NH₂-MIL-125(Ti) membranes prepared under single-mode microwave irradiation could possibly be attributed to improved microwave field uniformity, enhanced nonthermal effects, and higher absorption efficiency\[14\]. The mechanism of single-mode microwave irradiation in modulating the microstructure of MOF membranes, however, merits further in-depth investigation.

We measured the volumetric flow rates of both single and mixed gases through c-oriented NH₂-MIL-125(Ti) membranes to investigate the effect of the preferred orientation on gas-separation performance (Figure 4; see also SI-12). It was observed that the ideal selectivity of H₂/CO₂, H₂/N₂, and H₂/CH₄ gas pairs reached 24.8, 10.4, and 11.2, respectively, which was far above their Knudsen selectivity. The H₂ permeability measured in gas mixtures under the same conditions was slightly lower than its single-gas permeability.
which could be attributed to competitive adsorption between gases towards NH$_2$-MIL-125(Ti) membranes. The ideal selectivity of the H$_2$/CO$_2$ gas pair in this study was not only remarkably higher than that of other neat NH$_2$-MIL-125(Ti) membranes under similar operating conditions (ca. 4 at R.T. and 1 bar),\textsuperscript{[24]} but also easily exceeded the 2008 Robeson upper-bound line (see SI-13).

The effect of operating temperature on the separation performance of c-oriented NH$_2$-MIL-125(Ti) membranes was further studied. Both H$_2$ permeability and mixed H$_2$/CO$_2$ selectivity depended on the operating temperature (see SI-14). It was found that the H$_2$ permeability continuously increased, while the mixed H$_2$/CO$_2$ selectivity slightly decreased upon elevating the operating temperature (from 30 to 210°C), which could be attributed to a gradually weakened affinity between CO$_2$ and amine functional groups in the MOF framework at higher temperature.\textsuperscript{[19]} Furthermore, the long-term stability of prepared NH$_2$-MIL-125(Ti) membranes was tested at 30°C and 1 bar. It was observed that the H$_2$/CO$_2$ selectivity increased slightly initially, and then remained almost unchanged (see SI-15). This result can be attributed to the strong interaction between -NH$_2$ functional groups in the NH$_2$-MIL-125(Ti) framework and CO$_2$ molecules below 90°C,\textsuperscript{[20]} which spontaneously creates spatial constraints and narrows the passage of molecular diffusion,\textsuperscript{[21]} thus leading to enhanced H$_2$/CO$_2$ selectivity. Furthermore, our study indicated that the NH$_2$-MIL-125(Ti) membranes even showed considerable thermal stability at 180°C and 1 bar (see SI-15). Excellent long-term operational stability of the NH$_2$-MIL-125(Ti) membranes suggests that they could serve as competent gas-separation membranes.

Strong adhesion of the MOF active layer to the substrate is of vital importance for practical applications. In this study the adhesion strength of the prepared c-oriented NH$_2$-MIL-125(Ti) membrane was further evaluated by sonication in distilled water for 1 h. For comparison, a twinned 2 μm thick NH$_2$-MIL-125(Ti) membrane derived from TPOT precursors was also subjected to sonication under identical conditions. Sonication treatment resulted in severe damage to the twinned NH$_2$-MIL-125(Ti) membrane and substantial amounts of NH$_2$-MIL-125(Ti) grains peeled off from the substrate (see SI-16). In contrast, the c-oriented 0.5 μm thick NH$_2$-MIL-125(Ti) membrane derived from layered TiS$_2$ precursors remained relatively intact, which was a clear demonstration of its excellent mechanical stability.

To validate the reproducibility of this approach, six membranes were prepared and measured in parallel. Among them, four NH$_2$-MIL-125(Ti) membranes showed considerable H$_2$/CO$_2$ selectivity (> 20), thus indicating that the synthetic protocol was robust in terms of reproducibility (see SI-17). In addition to porous α-Al$_2$O$_3$ substrates, we further succeeded in the preparation of well-intergrown and highly c-oriented NH$_2$-MIL-125(Ti) films on nonporous glass plates (see SI-18), thus demonstrating the generality of this route.

To summarize, in this study, highly c-oriented NH$_2$-MIL-125(Ti) membranes were successfully prepared by combining oriented seeding with controlled in-plane epitaxial growth. A novel dynamic air–liquid interface-assisted self-assembly method was developed for the deposition of closely packed and highly c-oriented NH$_2$-MIL-125(Ti) monolayers on porous α-Al$_2$O$_3$ substrates, while the use of layered TiS$_2$ as the metal source and the employment of single-mode microwave irradiation during epitaxial growth were found to be indispensable for maintaining the desired in-plane growth and suppressing the undesired twin growth. A detailed investigation of microstructural differences between NH$_2$-MIL-125(Ti) membranes synthesized under single-mode and multi-mode microwave heating was carried out. Prepared c-oriented NH$_2$-MIL-125(Ti) membranes exhibited superior H$_2$/CO$_2$ selectivity as compared to randomly oriented membranes, thus demonstrating the importance of preferred-orientation control and twin-growth suppression in improving the separation performance of MOF membranes. The prepared NH$_2$-MIL-125(Ti) membranes showed excellent mechanical stability, which would be advantageous for practical applications. It is anticipated that the concepts revealed in this study could be illustrative for advancing the further development of MOF membranes in the future.

**Experimental Section**

Synthesis of NH$_2$-MIL-125(Ti) seeds: 2.5-Diamo-no-1,4-benzene-dicarboxylic acid (NH$_2$-BDC; 99%, Alfa Aesar; 1.12 g) and titanium isopropoxide (TPOT; 99.9%, Sigma–Aldrich; 0.2 mL) were dissolved in a solution containing DMF (99.8%, Shanghai Chemical Reagent Inc.; 27 mL) and dry methanol (99.5%, Shanghai Chemical Reagent Inc.; 3 mL) with stirring. The mixture was then transferred to a 50 mL Teflon-lined autoclave and solvothermally treated at 150°C under static conditions for 24 h. After cooling down, the solid product was centrifuged, washed with DMF/methanol, and dried in an oven at 60°C overnight.

$c$-Oriented NH$_2$-MIL-125(Ti) seed layer deposition: Prior to seed deposition, 0.04 g of prepared NH$_2$-MIL-125(Ti) microcrystals were mixed with ethanol (5 mL) and stirred in a cone-shaped bottle at room temperature for more than 6 days before use. Subsequently, an...
\(\alpha\text{-AlO}_3\) plate (Fraunhofer IKT, Germany) with a diameter of 18 mm, thickness of 1 mm, and pore size of 70 nm in the top layer was placed on a horizontal plane, and the top of the needle was held at the turbulent air-liquid interface (by using a circular pump), where the \(\text{NH}_2\text{-MIL-125}(\text{Ti})\)-containing ethanol suspension was injected at a speed of 2 \(\mu\text{L}\text{ min}^{-1}\). Finally, a closely packed and highly \(\alpha\text{-AlO}_3\) substrate. An identical procedure was employed for self-assembling \(\text{NH}_2\text{-MIL-125}(\text{Ti})\) monolayer on glass plates.

Secondary growth of \(\text{c-oriented NH}_2\text{-MIL-125}(\text{Ti})\) membranes by single-mode microwave heating with TiS as the titanium source: \(\text{NH}_2\text{-BDC} (0.28 \text{ g})\) and TiS (98%, Sigma-Aldrich; 0.007 g) were dissolved in a mixture of DMF (15 mL) and dry MeOH (15 mL) with stirring. The \(\text{NH}_2\text{-MIL-125}(\text{Ti})\) seed-layer-modified substrate was then placed vertically in an 80 mL glass vessel. The precursor solution was poured into the vessel, and the vessel was sealed and heated in a single-mode microwave oven (Discover, CEM) at 160°C for 10 min. After cooling to room temperature, the membrane was taken out, washed with copious amounts of methanol, and dried overnight.

Multi-mode microwave heating (CEM Mars 6) was also employed in the secondary growth of \(\text{NH}_2\text{-MIL-125}(\text{Ti})\) membranes with other synthetic conditions remaining unchanged.

Secondary growth of \(\text{NH}_2\text{-MIL-125}(\text{Ti})\) membranes by conventional heating with TiS as the titanium source: \(\text{NH}_2\text{-BDC} (0.28 \text{ g})\) and TPOT (0.02 mL) were dissolved in a mixture of DMF (15 mL) and dry methanol (15 mL) with stirring. Then the \(\text{NH}_2\text{-MIL-125}(\text{Ti})\) seed-layer-modified substrate was placed vertically in a 30 mL Teflon-lined stainless vessel. The precursor solution was poured into the vessel, and the vessel was sealed and put in a convective oven preheated to 160°C. After 12 h, the vessel was taken out and naturally cooled to room temperature in air. Finally, the membrane was taken out, washed with copious amounts of methanol, and dried overnight.

Secondary growth of \(\text{NH}_2\text{-MIL-125}(\text{Ti})\) membranes by conventional heating with TiS as the titanium source: The procedure was similar to secondary growth by conventional heating with TPOT as the titanium source except that TiS (0.007 g) was used as the metal source instead of TPOT (0.02 mL).

Secondary growth of \(\text{NH}_2\text{-MIL-125}(\text{Ti})\) membranes by single-mode microwave heating with TPOT as the titanium source: The procedure was similar to secondary growth by single-mode microwave heating using TiS as titanium source except that TPOT (0.02 mL) was used as the metal source instead of TiS (0.007 g).

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### Conflict of interest

The authors declare no conflict of interest.

### Keywords

membranes · metal-organic frameworks · microwave heating · oriented growth · self-assembly

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