

MOF Membranes

International Edition: DOI: 10.1002/anie.201810088
German Edition: DOI: 10.1002/ange.201810088In-Plane Epitaxial Growth of Highly *c*-Oriented NH₂-MIL-125(Ti) Membranes with Superior H₂/CO₂ Selectivity

Yanwei Sun, Yi Liu, Jürgen Caro, Xinwen Guo, Chunshan Song,* and Yi Liu*

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 NH₂-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 NH₂-MIL-125-(Ti) seed monolayers, the use of layered TiS₂ 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 H₂/CO₂ selectivity of 24.8, which was 6.1 times higher than that of their randomly oriented counterparts under similar operating conditions.

Metal-organic framework (MOF)-based separation membranes have offered unprecedented opportunities for gas separation, such as H₂ purification, CO₂ 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 -Al₂O₃ 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.^[2c] 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 -Al₂O₃) has remained fairly low.^[1e,6] Therefore, a new synthetic route was urgently needed to address the above existing issues.

NH₂-MIL-125(Ti), one of the most widely studied Ti-MOFs, has emerged as a promising candidate^[7] for membrane-based CO₂ capture because of its high affinity for CO₂, 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 NH₂-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)

[*] Dr. Y. Sun, Dr. Y. Liu, Prof. Dr. X. Guo, Prof. Dr. C. Song, Prof. Dr. Y. Liu
State Key Laboratory of Fine Chemicals
School of Chemical Engineering, Dalian University of Technology
Linggong Road No. 2, Ganjingzi District, Dalian 116024 (China)
E-mail: diligenliu@dlut.edu.cn

Prof. Dr. J. Caro
Institute of Physical Chemistry and Electrochemistry
Leibniz Universität Hannover
Callinstrasse 3A, 30167 Hannover (Germany)

Prof. Dr. X. Guo, Prof. Dr. C. Song
PSU-DUT Joint Centre for Energy Research
School of Chemical Engineering, Dalian University of Technology
Linggong Road NO. 2, Ganjingzi District, Dalian 116024 (China)
E-mail: csong@psu.edu

Prof. Dr. C. Song
EMS Energy Institute
Department of Energy and Mineral Engineering and Department of
Chemical Engineering, The Pennsylvania State University
University Park, PA 16802 (USA)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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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.^[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.^[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 NH₂-MIL-125(Ti) membranes.

In general, two modes of microwave heating exist, that is, single-mode and multi-mode.^[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 NH₂-MIL-125(Ti) membranes on porous α -Al₂O₃ 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 TiS₂ 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).

NH₂-MIL-125(Ti) seeds were synthesized by a simple solvothermal method.^[8b] Prepared NH₂-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, NH₂-MIL-125(Ti) seeds were stirred continuously in ethanol until uniformly dispersed.

The first step involved the oriented deposition of a NH₂-MIL-125(Ti) monolayer (see SI-3). Before deposition, a rectangular container was filled with DI water. The NH₂-MIL-125(Ti)-containing ethanol suspension was slowly injected at the turbulent air–liquid interface with a microsyringe until the final formation of a closely packed and highly *c*-oriented NH₂-

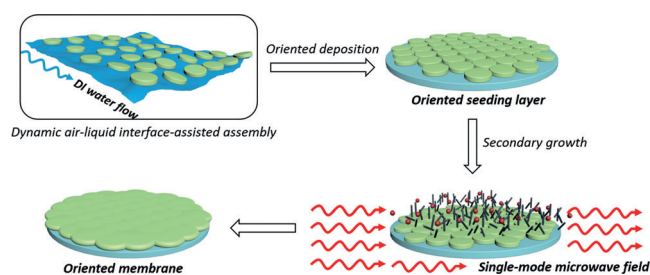


Figure 1. Procedure for the preparation of highly *c*-oriented NH₂-MIL-125(Ti) membranes by combining oriented seeding and controlled in-plane secondary growth (red spheres: Ti⁴⁺ ions, black rods: NH₂-BDC).

MIL-125(Ti) monolayer, which could be readily transferred to the porous α -Al₂O₃ substrate. SEM results indicated that the prepared NH₂-MIL-125(Ti) monolayer was uniform and closely packed (Figure 2a). Moreover, it was observed that

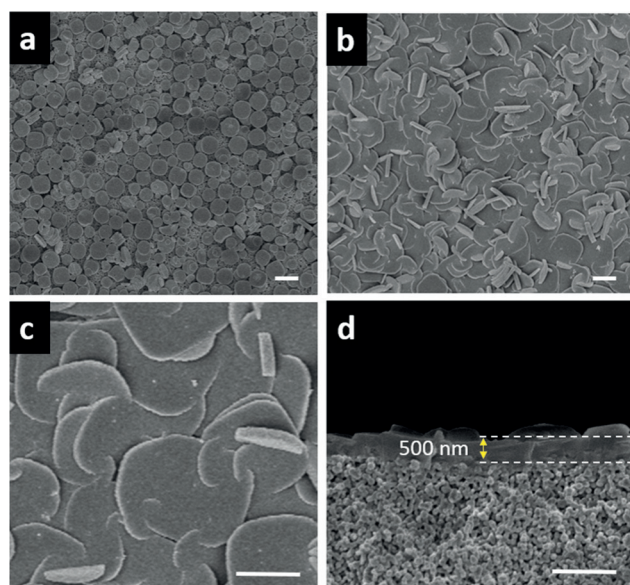


Figure 2. SEM images of a) the prepared NH₂-MIL-125(Ti) seed layer; b, c) the top and d) a cross-section of the prepared NH₂-MIL-125(Ti) membrane after secondary growth on the α -Al₂O₃ substrate. Scale bar: 1 μ m.

almost all NH₂-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 (001) diffraction peaks survived in the XRD pattern (Figure 3b). In contrast to MFI-type zeolites,^[9a] 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 NH₂-MIL-125(Ti) seeds into a closely packed and *c*-oriented monolayer; otherwise, NH₂-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 NH₂-MIL-125(Ti) seeds (see SI-4).

Besides ethanol, various other solvents, including methanol, *n*-*i*-propanol, *n*-butanol, acetone, and dichloromethane,

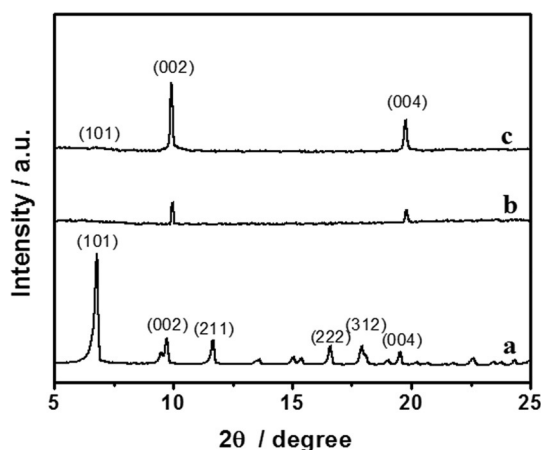


Figure 3. XRD patterns of a) $\text{NH}_2\text{-MIL-125(Ti)}$ powders, b) the prepared $\text{NH}_2\text{-MIL-125(Ti)}$ seed layer, and c) the prepared $\text{NH}_2\text{-MIL-125(Ti)}$ membrane after secondary growth on the $\alpha\text{-Al}_2\text{O}_3$ substrate.

were also employed as dispersants of $\text{NH}_2\text{-MIL-125(Ti)}$ microcrystals (see SI-5). However, the prepared $\text{NH}_2\text{-MIL-125(Ti)}$ monolayers were either loosely packed or not preferentially *c*-oriented. The superior microstructure of $\text{NH}_2\text{-MIL-125(Ti)}$ monolayers obtained by the use of ethanol dispersant could possibly be attributed to a superior monodispersity of $\text{NH}_2\text{-MIL-125(Ti)}$ microcrystals within ethanol and appropriate hydrophobicity/water solubility of ethanol, as evidenced in previous studies.^[11]

Although reflux,^[12] manual rubbing,^[13] and sonication^[14] have proven effective for the organization of highly *b*-oriented MFI monolayers, these methods could not be applied to oriented MOF seed layer assembly, owing to the lower mechanical, thermal and hydrothermal/solvothermal stability. For example, we found that $\text{NH}_2\text{-MIL-125(Ti)}$ microcrystals were prone to smash into pieces during manual assembly on glass substrates (see SI-6). The turbulent ALIAS method described above was more appropriate for the oriented organization of fragile MOF seeds owing to the mild operating conditions.

The next step was the controlled in-plane growth of *c*-oriented $\text{NH}_2\text{-MIL-125(Ti)}$ monolayers. Initially, titanium isopropoxide (TPOT), which has commonly been employed for the synthesis of Ti-MOFs, was used as the titanium source under conventional hydrothermal heating. However, it was observed that substantial amounts of twin crystals were formed simultaneously (see SI-7), even though synthetic conditions have been substantially optimized (see SI-8). Furthermore, the prepared $\text{NH}_2\text{-MIL-125(Ti)}$ membrane became too thick (ca. 2 μm). Such a phenomenon was also observed in the epitaxial growth of *b*-oriented MFI seed layers,^[9c,e,12] and the generation of undesired twins could be attributed to unavoidable nucleation of MFI crystals in the bulk precursor solution during epitaxial growth.^[9c,15] Therefore, by analogy, it was indispensable to suppress substantially the bulk nucleation of $\text{NH}_2\text{-MIL-125(Ti)}$ crystals during epitaxial growth so that undesired twin growth may be alleviated.

Our recent study showed that solid layered titanium disulfide (TiS_2) could serve as an efficient metal source for the synthesis of $\text{NH}_2\text{-MIL-125(Ti)}$ powders.^[16] As compared with the commonly used TPOT reagent, layered TiS_2 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,17] layered TiS_2 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 $\text{NH}_2\text{-MIL-125(Ti)}$ membranes. SEM images indicated that after secondary growth, well-intergrown $\text{NH}_2\text{-MIL-125(Ti)}$ membranes with few twin crystals had formed on porous $\alpha\text{-Al}_2\text{O}_3$ substrates (Figure 2b,c). A cross-sectional image further indicated that prepared $\text{NH}_2\text{-MIL-125(Ti)}$ 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 $\text{NH}_2\text{-MIL-125(Ti)}$ top layer and the porous $\alpha\text{-Al}_2\text{O}_3$ substrate (see SI-9), thus indicating that the $\text{NH}_2\text{-MIL-125(Ti)}$ layer did not penetrate into the substrate. The XRD pattern (Figure 3c) of prepared $\text{NH}_2\text{-MIL-125(Ti)}$ membrane further showed strong (002) and (004) reflections at 2θ values of 10.3 and 20.6°, respectively, which unambiguously demonstrated that the $\text{NH}_2\text{-MIL-125(Ti)}$ 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 $\text{NH}_2\text{-MIL-125(Ti)}$ 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 TiS_2 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 $\text{NH}_2\text{-MIL-125(Ti)}$ membranes be obtained. In contrast, the size of $\text{NH}_2\text{-MIL-125(Ti)}$ 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 $\text{NH}_2\text{-MIL-125(Ti)}$ membranes prepared under single-mode microwave irradiation could possibly be attributed to improved microwave field uniformity, enhanced nonthermal effects, and higher absorption efficiency.^[18] 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 $\text{NH}_2\text{-MIL-125(Ti)}$ 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 H_2/CO_2 , H_2/N_2 , and H_2/CH_4 gas pairs reached 24.8, 10.4, and 11.2, respectively, which was far above their Knudsen selectivity. The H_2 permeability measured in gas mixtures under the same conditions was slightly lower than its single-gas permeability,

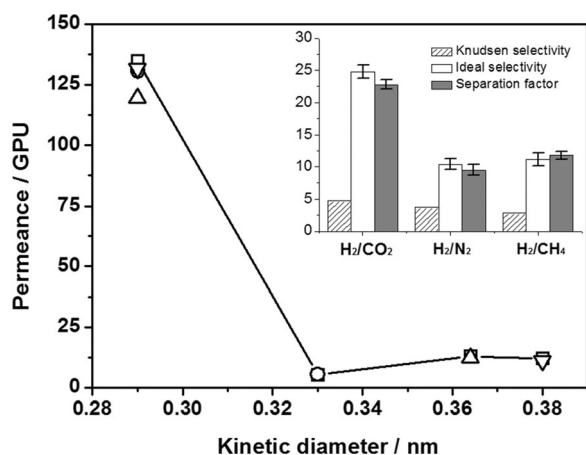


Figure 4. Permeability of single gases (□) and equimolecular H₂/CO₂ (○), H₂/N₂ (△), and H₂/CH₄ (▽) mixtures through the prepared NH₂-MIL-125(Ti) membrane at 30 °C as a function of the molecular kinetic diameter. The inset shows the Knudsen selectivity, ideal gas selectivity, and separation factor of H₂ over other gas molecules. Selectivity values are averaged over four membranes, and error bars correspond to the standard deviation.

which could be attributed to competitive adsorption between gases towards NH₂-MIL-125(Ti) membranes. The ideal selectivity of the H₂/CO₂ gas pair in this study was not only remarkably higher than that of other neat NH₂-MIL-125(Ti) membranes under similar operating conditions (ca. 4 at R.T. and 1 bar),^[7a] 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 NH₂-MIL-125(Ti) membranes was further studied. Both H₂ permeability and mixed H₂/CO₂ selectivity depended on the operating temperature (see SI-14). It was found that the H₂ permeability continuously increased, while the mixed H₂/CO₂ selectivity slightly decreased upon elevating the operating temperature (from 30 to 210 °C), which could be attributed to a gradually weakened affinity between CO₂ and amine functional groups in the MOF framework at higher temperature.^[19] Furthermore, the long-term stability of prepared NH₂-MIL-125(Ti) membranes was tested at 30 °C and 1 bar. It was observed that the H₂/CO₂ selectivity increased slightly initially, and then remained almost unchanged (see SI-15). This result can be attributed to the strong interaction between –NH₂ functional groups in the NH₂-MIL-125(Ti) framework and CO₂ molecules below 90 °C,^[20] which spontaneously creates spatial constraints and narrows the passage of molecular diffusion,^[21] thus leading to enhanced H₂/CO₂ selectivity. Furthermore, our study indicated that the NH₂-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 NH₂-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 NH₂-MIL-125(Ti) membrane was further evaluated by sonication in distilled water for 1 h. For comparison, a twinned 2 μm thick

NH₂-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 NH₂-MIL-125(Ti) membrane and substantial amounts of NH₂-MIL-125(Ti) grains peeled off from the substrate (see SI-16). In contrast, the *c*-oriented 0.5 μm thick NH₂-MIL-125(Ti) membrane derived from layered TiS₂ 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 NH₂-MIL-125(Ti) membranes showed considerable H₂/CO₂ selectivity (> 20), thus indicating that the synthetic protocol was robust in terms of reproducibility (see SI-17). In addition to porous α-Al₂O₃ substrates, we further succeeded in the preparation of well-intergrown and highly *c*-oriented NH₂-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 NH₂-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 NH₂-MIL-125(Ti) monolayers on porous α-Al₂O₃ substrates, while the use of layered TiS₂ 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 NH₂-MIL-125(Ti) membranes synthesized under single-mode and multi-mode microwave heating was carried out. Prepared *c*-oriented NH₂-MIL-125(Ti) membranes exhibited superior H₂/CO₂ 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 NH₂-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 NH₂-MIL-125(Ti) seeds: 2,5-Diamino-1,4-benzene-dicarboxylic acid (NH₂-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 NH₂-MIL-125(Ti) seed layer deposition:** Prior to seed deposition, 0.04 g of prepared NH₂-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

α -Al₂O₃ plate (Fraunhofer IKTS, 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 NH₂-MIL-125(Ti)-containing ethanol suspension was injected at a speed of 2 μ L min⁻¹. Finally, a closely packed and highly *c*-oriented NH₂-MIL-125(Ti) monolayer was spontaneously formed at the air–liquid interface and transferred to the porous α -Al₂O₃ substrate. An identical procedure was employed for self-assembling NH₂-MIL-125(Ti) seeds on glass plates.

Secondary growth of *c*-oriented NH₂-MIL-125(Ti) membranes by single-mode microwave heating with TiS₂ as the titanium source: NH₂-BDC (0.28 g) and TiS₂ (98%, Sigma–Aldrich; 0.007 g) were dissolved in a mixture of DMF (15 mL) and dry MeOH (15 mL) with stirring. The NH₂-MIL-125(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 NH₂-MIL-125(Ti) membranes with other synthetic conditions remaining unchanged.

Secondary growth of NH₂-MIL-125(Ti) membranes by conventional heating with TPOT as titanium source: NH₂-BDC (0.28 g) and TPOT (0.02 mL) were dissolved in a mixture of DMF (15 mL) and dry methanol (15 mL) with stirring. Then the NH₂-MIL-125(Ti) seed-layer-modified substrate was placed vertically in a 50 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 NH₂-MIL-125(Ti) membranes by conventional heating with TiS₂ as the titanium source: The procedure was similar to secondary growth by conventional heating with TPOT as the titanium source except that TiS₂ (0.007 g) was used as the metal source instead of TPOT (0.02 mL).

Secondary growth of NH₂-MIL-125(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 TiS₂ as titanium source except that TPOT (0.02 mL) was used as the metal source instead of TiS₂ (0.007 g).

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Conflict of interest

The authors declare no conflict of interest.

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