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Authors: Yanwei Sun, Yi Liu, Juergen Caro, Xinwen Guo, Chunshan Song, and Yi Liu

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In-Plane Epitaxial Growth of Highly *c*-Oriented NH₂-MIL-125(Ti) Membranes with Superior H₂/CO₂ Selectivity

Yanwei Sun,[a] Yi Liu,[a] Jürgen Caro,[b] Xinwen Guo,[a, c] Chunshan Song,*[a, c, d] Yi Liu*[a]

Abstract: Preferred orientation control has significant impacts on separation performance of MOF membranes. Nevertheless, under most conditions preferred orientation of MOF membranes is dominated by 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 metal precursors and the employment of single-mode microwave heating were found to be crucial for ensuring the preferred *c*-orientation while simultaneously suppressing the undesired twin growth. Owing to the reduced grain boundary defects, prepared *c*-oriented NH₂-MIL-125(Ti) membranes showed an ideal H₂/CO₂ selectivity of 24.8, which was 6.1 times higher than 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 performances by ordered arrangement of nanopores, decrease of grain boundary defects and reduction in diffusion path lengths.[2] Although diverse methods have been developed for production of well-intergrown MOF membranes, elaborate orientation control of their preferred orientation remined a very challenging task. [2a,3] For instance, *in situ* growth method usually led to the formation of random-oriented MOF membranes rather than oriented ones[4] since in general, nucleation and crystallization of MOF particles occurred simultaneously in the bulk solution and on the substrate surface, therefore making precise orientation control particularly challenging except on rare occasions. In contrast, secondary growth was enabled to exert
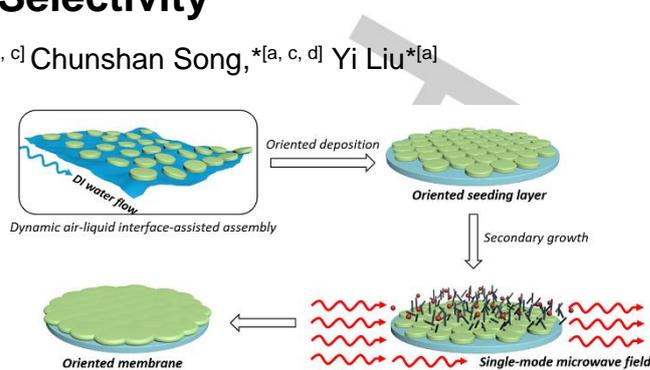
[a]   Dr. Y. Sun, Dr. Y. Liu, Prof. Dr. X. Guo, Prof. Dr. C. Song, Prof. Dr. Y. Liu
        State Key Laboratory of Fine Chemicals
        School of Chemical Engineering, Dalian University of Technology
        Linggong Road NO. 2, Ganjingzi District, Dalian 116023 (China)
        E-mail: diligenliu@dlut.edu.cn
[b]   Prof. Dr. J. Caro
        Institute of Physical Chemistry and Electrochemistry, Leibniz Universität Hannover
        Callinstrasse 3A, 30167 Hannover (Germany)
[c]   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 116023 (China)
        Email: csong@psu.edu
[d]   Prof. Dr. C. Song
        EMS Energy Institute
        Departments of Energy and Mineral Engineering and of Chemical Engineering. The Pennsylvania State University
        University Park, PA, 16802 (USA)

Figure 1. Schematic illustration of the preparation procedure of highly *c*-oriented NH₂-MIL-125(Ti) membrane by combining oriented seeding and controlled in-plane secondary growth (Red sphere: Ti⁺⁴ ion, black rod: NH₂-BDC).

more precise control over preferred orientation of MOF membranes by combining pre-deposition of oriented MOF seed layers with controlled in-plane epitaxial growth. Nevertheless, being analogous to oriented zeolite membrane synthesis, several technical obstacles were still waiting to be solved before full utilization of this method: 1) Oriented MOF seed layer deposition. Lai *in situ* deposited preferentially (102) oriented MOF-5 seed layers on α-Al₂O₃ substrates with microwave-induced thermal deposition method,[5] and Wang successfully attached plate-like ZIF-L seeds to substrates along *c*-axis via vacuum filtration in the presence of polyethyleneimine.[2c] Nevertheless, facile organization of anisotropic MOF seeds with decent aspect ratios (like coffin-shaped MOF crystals) into highly oriented monolayers on porous substrates remained a challenging task. 2) Controlled in-plane secondary growth. As shown below, it remained a challenging task to suppress undesired twin growth, which may severely deteriorate the separation performance, owing to the difficulty in effective suppression of bulk nucleation occurring simultaneously. 3) Maintaining high adhesion strength. Compared with *in situ* solvothermal growth, the adhesion strength between MOF layers prepared by secondary growth and porous ceramic substrates (like α-Al₂O₃) remained fairly low.[1e,6] Therefore, new synthetic route was urgently needed to solve the above existing issues.

NH₂-MIL-125(Ti) as one of the most widely studied Ti-MOFs has merged as a promising candidate [7] for membrane-based CO₂ capture due to the high affinity for CO₂, high thermal stability and straight nanochannels along the *c*-axis, which was advantageous for reduction of diffusion paths.[8] Therefore, fabrication of highly *c*-oriented NH₂-MIL-125(Ti) membrane was highly desirable due to the potential for reduction of diffusion barriers and elimination of grain boundary defects.

Being analogous to MOFs, in recent decades significant progress was also made in fabrication of oriented zeolite membranes (in particular *b*-oriented MFI zeolite membranes). For instance, 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 the geometric factor and intrinsic hydrophobicity of anisotropic MFI microcrystals.[9a,9b] Second, microwave-assisted hydrothermal
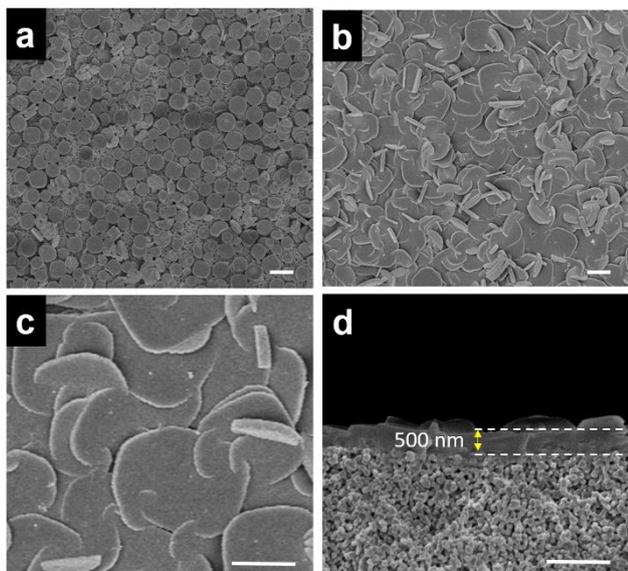
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Figure 2. SEM images of a) prepared NH$_2$-MIL-125(Ti) seed layer; b, c) top and d) cross-section of prepared NH$_2$-MIL-125(Ti) membrane after secondary growth on the α-Al$_2$O$_3$ substrate. Scale bar: 1 µm.

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

*C*method was employed to maintain the desired in-plane epitaxial growth while simultaneously suppress the undesired twin growth, relying on the unique nucleation-related bottle-neck effect of microwave irradiation.[9e] Considering the similarity between MOFs and zeolites, it is expected that our experience could provide insights into fabrication of well-intergrown and highly *c*-oriented NH$_2$-MIL-125(Ti) membranes.

It is particularly noted that in general, two modes, i.e., single-mode and multi-mode, exist in the case of microwave heating.[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 yielding a high-density microwave field. In contrast, the 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 leading to a heterogeneous heating profile. At present, multi-mode microwave heating has been widely applied in hydrothermal/solvothermal of molecular sieve membranes. Potential applications of single-mode microwave heating, however, has been rarely explored in this field. Consideration that single-mode microwave heating is advantageous over its multi-mode counterpart in terms of microwave field uniformity and intensity, it is expected that remarkably enhanced non-thermal effects and higher absorption efficiency can be achieved which may potentially lead to improved microstructure in case 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 experimental section and SI-1). Among various factors, the use of turbulent DI water layers as temporary soft substrates during the oriented seeding process,
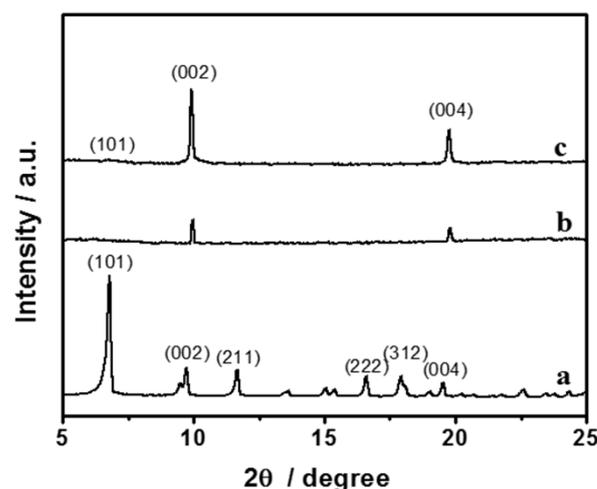
the employment of layered TiS$_2$ as titanium precursors and single-mode microwave reactor during the in-plane epitaxial growth process were found to be essential for achieving the desired microstructure.

NH$_2$-MIL-125(Ti) seeds were synthesized by a simple solvothermal method.[8b] As shown in SI-2, prepared NH$_2$-MIL-125(Ti) seeds were highly uniform (~800 nm in length and ~200 nm in thickness) and exhibited circular plate morphology. Prior to oriented deposition, NH$_2$-MIL-125(Ti) seeds were added in ethanol solvent and unceasingly stirred until uniformly dispersed. The first step involved oriented deposition of a NH$_2$-MIL-125(Ti) monolayer (illustrated in SI-3). Before deposition, a rectangular container was filled with DI water. The NH$_2$-MIL-125(Ti)-containing ethanol suspension was slowly injected at the turbulent air-liquid interface with a micro-syringe until the final formation of a closely packed and highly *c*-oriented NH$_2$-MIL-125(Ti) monolayer, which could be easily transferred on the porous α-Al$_2$O$_3$ substrate. SEM results indicated that 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 closely contacted with each other. XRD patterns further confirmed the dominance of a preferred *c*-orientation since only (00l) diffraction peaks survived in the XRD pattern (shown in Figure 3b). It should be emphasized that different from MFI-type zeolites,[9a] herein maintaining the air-liquid interface in a turbulent state with a circulating water pump is of vital importance to promote organization of NH$_2$-MIL-125(Ti) seeds into a closely packed and *c*-oriented monolayer; or else, 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 (SI-4).

In addition to ethanol, various other solvents, including methanol, *n*-/*i*-propanol, *n*-butanol, acetone and dichloromethane, were also employed as dispersants of NH$_2$-MIL-125(Ti) microcrystals (SI-5). Nevertheless, prepared NH$_2$-MIL-125(Ti) monolayers were either loosely packed or not preferentially *c*-oriented. Superior
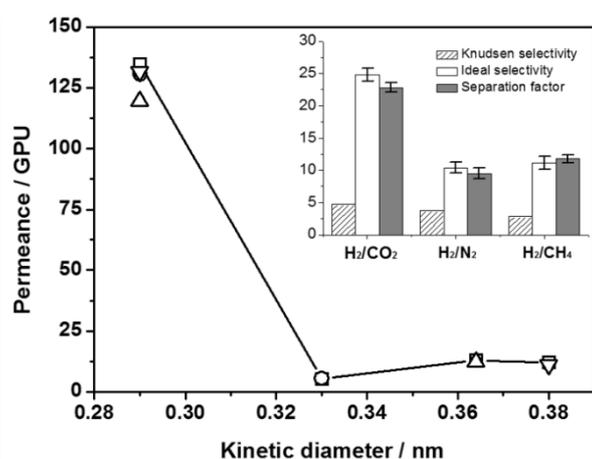
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Figure 4. Permeabilities of single gases ($\square$) and equimolecular H_2/CO_2 ($\bigcirc$), H_2/N_2 ($\triangle$) and H_2/CH_4 ($\triangledown$) mixtures through prepared NH_2-MIL-125(Ti) membrane at 30 °C as a function of molecular kinetic diameters. The inset shows the Knudsen selectivity, ideal gas selectivity and separation factor of H_2 over other gas molecules. Note: Selectivity values are averaged over four membranes and error bars correspond to the standard deviation.

microstructure of NH_2-MIL-125(Ti) monolayers obtained by the use of ethanol dispersant could possibly be attributed to a superior mono-dispersity of NH_2-MIL-125(Ti) microcrystals within ethanol and appropriate hydrophobicity/water solubility of ethanol as evidenced in previous literature.[11]

It should be emphasized that although reflux,[12] manual rubbing[13] and sonication[14] have proven effective for organization of highly *b*-oriented MFI monolayers, above-mentioned methods could not apply to oriented MOF seed layer assembly, owing to the lower mechanical, thermal and hydrothermal/solvothermal stability. For instance, we found that NH_2-MIL-125(Ti) microcrystals were prone to smash into pieces during manual assembly on glass substrates (SI-6). In comparison, above-mentioned turbulent ALIAS method was more appropriate for oriented organization of fragile MOF seeds due to a mild operating condition.

The next step referred to controlled in-plane growth of *c*-oriented NH_2-MIL-125(Ti) monolayers. Initially titanium isopropoxide (TPOT), which was commonly employed for 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 (SI-7), even though the synthetic condition had been substantially optimized (SI-8). In addition, prepared NH_2-MIL-125(Ti) membrane became too thick (~2 μm). Such phenomenon was also observed in epitaxial growth of *b*-oriented MFI seed layers,[9c,9e,12] and the generation of undesired twins could be attributed to unavoidable nucleation of MFI crystals in the bulk precursor solution during epitaxial growth.[9e,15] Therefore, it became indispensable to suppress substantially the bulk nucleation of NH_2-MIL-125(Ti) crystals during epitaxial growth so that the undesired twin growth may be alleviated by analogy.

Our recent study showed that solid layered titanium disulfide (TiS_2) could serve as efficient metal source for the synthesis of NH_2-MIL-125(Ti) powders.[16] Compared with the commonly used TPOT reagent, layered TiS_2 dissolved in the precursor solution more slowly and homogenously under solvothermal conditions, which was potentially advantageous for suppression of the

undesired twin growth. Furthermore, relying on the unique nucleation-related bottleneck effect of microwave irradiation,[9e,17] in this study, layered TiS_2 was used as the metal source and single-mode microwave heating was employed for more effective suppression of bulk nucleation during epitaxial growth of NH_2-MIL-125(Ti) membranes. SEM images indicated that after secondary growth, well-intergrown NH_2-MIL-125(Ti) membranes with few twin crystals had been formed on porous α-Al_2O_3 substrates (Figure 2b, c). Cross-sectional image further indicated that prepared NH_2-MIL-125(Ti) membranes were ~0.5 μm thick (Figure 2d). EDXS pattern of the cross-section further showed that there existed a sharp boundary between the NH_2-MIL-125(Ti) top layer and the porous α-Al_2O_3 substrate (SI-9), indicating that the NH_2-MIL-125(Ti) layer did not penetrate into the substrate. XRD pattern (Figure 3c) of prepared NH_2-MIL-125(Ti) membranes further showed strong (002) and (004) reflections at 2θ values of 10.3° and 20.6° respectively, which unambiguously demonstrated that the NH_2-MIL-125(Ti) layer was indeed dominantly *c*-oriented. In addition, there was a very weak diffraction peak located at the 2θ value of 6.7°, which was assigned to the (101) crystal plane of NH_2-MIL-125(Ti) phase, as shown in Figure 3c. The low intensity of other diffraction peaks vividly demonstrated the presence of rare twin crystals.

It is noteworthy that the simultaneous use of layered TiS_2 as metal source and employing single-mode microwave heating is indispensable to maintain the desired in-plane epitaxial growth; otherwise, the undesired twin growth could not be effectively suppressed (SI-10). Moreover, it is interesting to note that only by single-mode microwave heating well-intergrown NH_2-MIL-125(Ti) membranes could be obtained. In contrast, the size of NH_2-MIL-125(Ti) seeds only slightly increased and substantial inter-crystal defects existed in the case of multi-mode microwave heating (SI-11). To the best of our knowledge, this represents the first report of single-mode microwave-assisted hydrothermal/solvothermal synthesis of molecular sieve membranes. The superior microstructure for NH_2-MIL-125(Ti) membranes prepared under single-mode microwave irradiation could possibly be attributed to improved microwave field uniformity, enhanced non-thermal effects and higher absorption efficiency.[18] The mechanism of single-mode microwave irradiation in modulating microstructure of MOF membranes, however, merits further in-depth investigation.

Consequently, volumetric flow rates of both single and mixed gases through *c*-oriented NH_2-MIL-125(Ti) membranes were measured in an attempt to investigate the effect of preferred orientation on gas separation performances (shown in Figure 4 and 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. Simultaneously, the H_2 permeability measured in gas mixtures under the same condition was slightly lower than its single gas permeability, which could be attributed to a competitive adsorption between gases towards NH_2-MIL-125(Ti) membranes. It was noted that 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 (~4 at R.T. and 1 bar),[7a] but also easily exceeded the 2008 Robeson upper-bound line (SI-13).

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The effect of operating temperature on the separation performance of *c*-oriented NH_2-MIL-125(Ti) membranes was further studied. Dependence of both H_2 permeability and mixed H_2/CO_2 selectivity on the operating temperature was illustrated in SI-14. It was found that the H_2 permeability unceasingly increased while the mixed H_2/CO_2 selectivity was slightly decreased upon elevating the operating temperature (from 30 to 210 ^{o}C), which could be attributed to a gradually weakened affinity between CO_2 and amine functional groups in the MOF framework at higher temperature.[19] In addition, the long-term stability of prepared NH_2-MIL-125(Ti) membrane was tested at 30 ^{o}C and 1 bar. It was observed that initially the H_2/CO_2 selectivity slightly increased, and then became almost unchanged (shown in SI-15). This 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 ^{o}C [20] which spontaneously creates spatial constraint and narrows the passage of molecular diffusion[21] leading to an 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 ^{o}C and 1 bar (shown in SI-15). Excellent long-term operation stability of the NH_2-MIL-125(Ti) membranes warrants that they can serve as competent gas separation membranes.

Strong adhesion of the MOF active layer to the substrate is of vital importance for practical applications. Herein the adhesion strength of prepared *c*-oriented NH_2-MIL-125(Ti) membrane was further evaluated by sonicating 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 scconication under identical conditions. As shown in SI-16, sonication treatment resulted in severe damage to the twinned NH_2-MIL-125(Ti) membrane and substantial NH_2-MIL-125(Ti) grains had peeled off from the substrate. 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 vivid demonstration of their 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), demonstrating that the synthetic protocol was robust in terms of reproducibility (shown in SI-17).

In addition to porous α-Al_2O_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 (shown in SI-18), 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 and controlled in-plane epitaxial growth. A novel dynamic air-liquid interface-assisted self-assembly method was developed for deposition of closely packed and highly *c*-oriented NH_2-MIL-125(Ti) monolayers on porous α-Al_2O_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 indispensable for maintaining the desired in-plane growth and suppressing the undesired twin growth. In particular, 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 compared with randomly oriented ones, therefore demonstrating the importance of preferred orientation control and twin growth suppression in improving the separation performance of MOF membranes. In addition, prepared NH_2-MIL-125(Ti) membranes showed excellent mechanical stability, which would be advantageous for their practical applications. It was anticipated that the concept, rule and approach revealed in this study could be illustrative for advancing further development of MOF membranes in the future.

Experimental Section

Synthesis of NH_2-MIL-125(Ti) seeds: 1.12 g 2,5-Diamino-1,4-benzenedicarboxylic acid (NH_2-BDC) (99%, Alfa Aesar) and 0.2 ml titanium isopropoxide (TPOT) (99.9%, Sigma-Aldrich) were dissolved in a solution containing 27 ml DMF (99.8%, Shanghai Chemical Reagent Inc.) and 3 ml dry methanol (99.5%, Shanghai Chemical Reagent Inc.) with stirring. The mixture was then transferred to a 50 ml Teflon-lined autoclave and solvothermally treated at 150 °C under static condition 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 prepared NH_2-MIL-125(Ti) microcrystals were mixed with 5 ml of ethanol and stirred in a cone-shaped bottle at room temperature for more than 6 days before use. Consequently, the α-Al_2O_3 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 onto a horizontal plane, and the top of the needle was held at the turbulent air-liquid interface (by using a circucccclar pump) where the NH_2-MIL-125(Ti)-containing ethanol suspension was injected at the speed of 2 µl min^{-1}. Finally, a closely packed and highly *c*-oriented NH_2-MIL-125(Ti) monolayer was spontaneously formed at air-liquid interface and transferred to the porous α-Al_2O_3 substrate. Identical procedure was employed for self-assembling NH_2-MIL-125(Ti) seeds on glass plates.

Secondary growth of *c*-oriented NH_2-MIL-125(Ti) membranes by single-mode microwave heating with TiS_2 as titanium source: 0.28 g NH_2-BDC and 0.007g TiS_2 (98%, Sigma-Aldrich) were dissolved in a solution containing 15 ml DMF and 15 ml dry MeOH with stirring. Then the NH_2-MIl-125(Ti) seed layer-modified substrate was vertically placed into a 80 ml glass vessel. After pouring the precursor solution into the vessel, the vessel was sealed and heated in a single-mode microwave oven (Discover, CEM) at 160 °C for 10 min. After cooling to R.T., the membrane was taken out, washed with copious methanol and dried overnight. In addition to single-mode microwave heating, multi-mode microwave heating (CEM Mars 6) was also employed in secondary growth of NH_2-MIL-125(Ti) membranes with other synthetic conditions remaining unchanged.

Secondary growth of NH_2-MIL-125(Ti) membranes by conventional heating with TPOT as titanium source: 0.28 g NH_2-BDC and 0.02 ml TPOT were dissolved in a solution containing 15 ml DMF and 15 ml dry methanol with stirring. Then the NH_2-MII-125(Ti) seed layer-modified substrate was vertically

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placed into a 50 ml Teflon-lined stainless vessel. After pouring the precursor solution into the vessel, the vessel was sealed and put into a convective oven with the temperature pre-heated to 160 °C. After an elapsed time of 12 h, the vessel was taken out and naturally cooled to R.T. in air. Finally, the membrane was taken out, washed with copious of methanol and dried overnight.

Secondary growth of NH_2-MIL-125(Ti) membranes by conventional heating with TiS_2 as titanium source: The procedure was similar to secondary growth by conventional heating with TPOT as titanium source except that 0.007g TiS_2 was used as metal source instead of 0.02 ml TPOT.

Secondary growth of NH_2-MIL-125(Ti) membranes by single-mode microwave heating with TPOT as titanium source: The procedure was similar to secondary growth by single-mode microwave heating using TiS_2 as titanium source except that 0.02 ml TPOT was used as metal source instead of 0.007g TiS_2.

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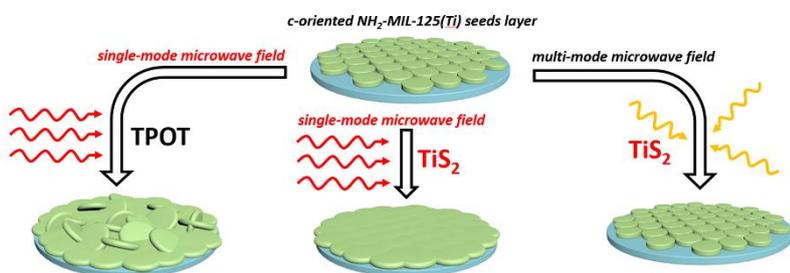
Conflict of interest

The authors declare no conflict of interest.

Keywords: membrane • metal organic framework • self-assembly • microwave heating • oriented growth

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

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In-Plane Epitaxial growth of Highly c-Oriented NH2-MIL-125(Ti) Membranes with Superior H2/CO2 Selectivity

Exerting precise control over the microstructure of MOF membrane remaines a challenging task. Herein we prepared well-intergrown highly *c*-oriented NH$_2$-MIL-125(Ti) membranes by innovating both seeding and secondary growth processes. A turbulent air-liquid interface method was developed for oriented deposition of *c*-oriented monolayer, while the use of layered TiS$_2$ as metal precursors and employment of single-mode microwave heating were indispensable for suppressing undesired twin growth during secondary growth. Prepared membrane showed superior H$_2$/CO$_2$ selectivity possibly due to reduced grain boundary defects.