

Concurrent Manipulation of Out-of-Plane and Regional In-Plane Orientations of NH₂-UiO-66 Membranes with Significantly Reduced Anisotropic Grain Boundary and Superior H₂/CO₂ Separation Performance

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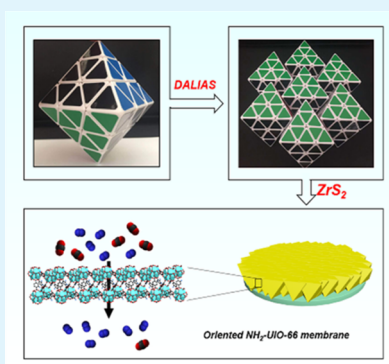
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Supporting Information

ABSTRACT: Preferred orientation has proven to exert a significant impact on the gas separation performance of metal–organic framework membranes. Nevertheless, realizing three-dimensional orientation control remains a challenging issue. In this study, well-intergrown NH₂-UiO-66 membranes with both (111) out-of-plane and regional in-plane orientations were prepared by combining oriented deposition of seeds and solvothermal epitaxial growth. Dynamic air–liquid interface-assisted self-assembly method was employed to organize uniform octahedral-shaped NH₂-UiO-66 seeds into closely packed monolayers with (111) out-of-plane and regional in-plane orientations, whereas the use of ZrS₂ as the zirconium precursor during the solvothermal epitaxial growth was found indispensable for sealing the intercrystalline gaps while preserving the preferred orientation inherited from seed layers. In addition, compared with solvothermal heating, employing microwave heating led to poor intergrowth between neighboring NH₂-UiO-66 crystals because of a lower dielectric loss factor of the reaction medium. Gas permeation results indicated that the prepared NH₂-UiO-66 membranes exhibited H₂/CO₂ selectivity up to 5.5 times higher than their counterparts with random and/or mere out-of-plane orientations as well as H₂ permeability 14.5 times higher than NH₂-MIL-125(Ti) membranes with mere out-of-plane orientation under similar operating conditions.

KEYWORDS: metal organic frameworks, membranes, orientation, epitaxial growth, self-assembly



1. INTRODUCTION

Metal–organic framework (MOF) membranes have shown great promise for energy-efficient gas separation and purification.^{1–12} Among all microstructural factors, grain orientation usually exerts great influence on their separation performance, owing to the ordered spatial arrangement of micropores, reduction in the grain boundary defect density, and decrease of the diffusion path length.^{13–18} Among the available methods for preferred orientation control, the oriented epitaxial growth method, which involved oriented deposition of MOF seed layers followed by epitaxial growth, exhibited obvious superiority in terms of generality, accuracy, and adaptability because of the decoupling of nucleation and epitaxial growth steps. With this method, diverse MOF membranes exhibiting a high degree of out-of-plane orientation were prepared.^{16,19–21} Nevertheless, concurrent manipulation of both out-of-plane and in-plane orientations of MOF membranes, which may further reduce crystallographic misorientations and defects at grain boundaries, remains a challenging issue. Increasing the grain size of MOF seeds represents an effective way to decrease the in-plane misorientation; nevertheless, the membrane thickness may also increase, which inevitably leads to increased diffusion

barriers for guest molecules. Alternatively, achieving regional in-plane orientation via deposition of MOF seed layers with both out-of-plane and regional in-plane orientations followed by in-plane epitaxial growth along the crystallographic direction inherited from MOF seed layers represents a more practical approach for decreasing the defects and misorientations at grain boundaries without significantly compromising diffusion barriers. The validity of this concept, however, has not been explicitly demonstrated yet.

In recent decades, UiO-66-type MOF materials with Zr₆O₄(OH)₄(BDC)₆ (BDC = 1,4-benzene-dicarboxylate) formula and FCU topology are believed to be promising candidates for separation membranes because of their superior chemical and thermal stabilities.^{22–26} NH₂-UiO-66 shares an identical topology with UiO-66 and consists of Zr₆O₄(OH)₄ clusters coordinated with 2-amino terephthalate. NH₂-UiO-66 has been considered as an ideal candidate for membrane-based

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H₂/CO₂ separation because of strong interactions between CO₂ molecules and amine functional groups in the framework;^{27–30} moreover, compared with other orientations, the (111) out-of-plane orientation enables quasi-vertical alignment of 5.7 Å-sized straight pores on porous substrates so that the shorter diffusion path length can be achieved.³¹ Combining with potential microstructural benefits derived from in-plane orientation, in this study, we aim to prepare well-intergrown NH₂-UiO-66 membranes with both (111) out-of-plane and regional in-plane orientations on porous α -Al₂O₃ substrates (schematically shown in Figure 1). Initially, uniform

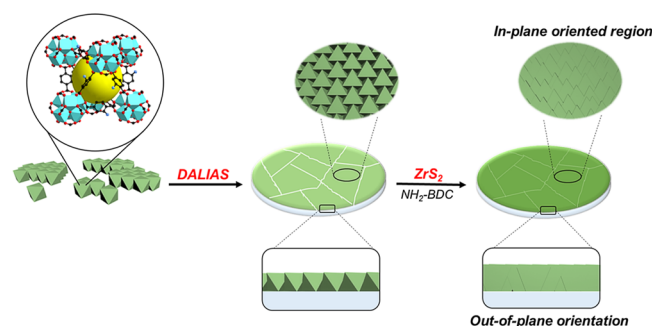


Figure 1. Schematic illustration of the preparation procedure of NH₂-UiO-66 membranes with both (111) out-of-plane orientation and regional in-plane orientation by combining oriented seeding and solvothermal epitaxial growth.

octahedral-shaped NH₂-UiO-66 seeds were prepared; consequently, a facile dynamic air–liquid interface self-assembly (DALIAS) method was employed to organize NH₂-UiO-66 seeds into closely packed monolayers with both (111) out-of-plane and regional in-plane orientations; finally, epitaxial solvothermal growth capable of sealing intercrystalline gaps while preserving orientations inherited from seed layers was conducted. To the best of our knowledge, this represents the first report of the fabrication of well-intergrown MOF membranes with both out-of-plane and regional in-plane orientations on porous substrates. Owing to the superior microstructural features, the prepared NH₂-UiO-66 membranes exhibited superior H₂/CO₂ separation performances compared with their counterparts with random and/or mere out-of-plane orientations.

2. EXPERIMENTAL SECTION

2.1. Materials. 2-Amino terephthalic acid (NH₂-BDC, 99.5%, Merck), disulfide zirconium (ZrS₂, 99.5%, Co., Ltd, Shanghai, China, AR), *N,N*-dimethylformamide (DMF, Tianjin kernel Chemical Research Agent Institute, AR), zirconium tetrachloride (ZrCl₄, 99.5%, Co., Ltd, ALADDIN Reagent, Shanghai, China, AR), acetic acid (AC, Tianjin kernel Chemical Research Agent Institute, AR), and polyvinylpyrrolidone (PVP, 99%, ALADDIN Reagent, Shanghai, China, AR) were used as received without further purification.

2.2. Solvothermal Synthesis of NH₂-UiO-66 Seeds. NH₂-BDC (216 mg, 0.6 mmol) and TEA (14 mg, 0.1 mmol) were added to 140 mL of DMF under stirring for 10 min before the addition of AC (20 mL, 0.36 mol). Consequently, the precursor solution was heated to 120 °C in an oil bath, and 10 mL of ZrCl₄ (280 mg, 0.6 mmol)-containing DMF was added. The reaction was maintained at 120 °C for 6 h. The obtained solid products were centrifuged at 8000 rpm for 5 min, washed with DMF and methanol three times, and finally dried at 100 °C for 12 h.

2.3. (111) Out-of-Plane and Regional In-Plane Oriented NH₂-UiO-66 Seed Layer Deposition. The seed layer deposition

process was similar to our previous report,²⁰ except that the disk-shaped NH₂-MIL-125(Ti) seeds were replaced by octahedral-shaped NH₂-UiO-66 seeds (40 mg), which were mixed with 5 mL of anhydrous ethanol containing 2 mg of PVP and sonicated for 1 h prior to use.

2.4. Epitaxial Growth of (111) Out-of-Plane and Regional In-Plane Oriented NH₂-UiO-66 Membrane by Conventional Heating with ZrS₂ as the Zirconium Source. NH₂-BDC (100 mg) and 80 mg of ZrS₂ (98%, Sigma-Aldrich) were dissolved in a solution containing 20 mL of DMF, 3 mL of AC, and 0.01 mL of deionized (DI) water. Then, the NH₂-UiO-66 seed layer-modified substrate was vertically placed into a 50 mL Teflon-lined autoclave, immersed in the precursor solution, and put into a convective oven. After solvothermal reaction at 160 °C for 24 h and cooling to room temperature, the membrane was rinsed with anhydrous methanol and dried for 12 h.

2.5. Epitaxial Growth of (111) Out-of-Plane and Regional In-Plane Oriented NH₂-UiO-66 Membrane by Single-Mode Microwave Heating with ZrS₂ as the Zirconium Source. NH₂-BDC (100 mg) and 80 mg of ZrS₂ were dissolved in a solution containing 20 mL of DMF, 3 mL of AC, and 0.01 mL of DI water. The procedure was similar to the epitaxial growth of NH₂-UiO-66 membrane by conventional heating, except that single-mode microwave heating (Discover, CEM) was employed, and the reaction time was set at 60 min.

2.6. Epitaxial Growth of (111) Out-of-Plane and Regional In-Plane Oriented NH₂-UiO-66 Membrane by Conventional Heating with ZrCl₄ as the Zirconium Source. The procedure was similar to epitaxial growth of NH₂-UiO-66 membrane by conventional heating with ZrS₂ as the zirconium source, except that 100 mg of ZrCl₄ was used instead of 80 mg of ZrS₂.

2.7. Epitaxial Growth of (111) Out-of-Plane and Regional In-Plane Oriented NH₂-UiO-66 Membrane by Single-Mode Microwave Heating with ZrCl₄ as the Zirconium Source. The procedure was similar to the epitaxial growth of NH₂-UiO-66 membrane by single-mode microwave heating with ZrS₂ as the zirconium source, except that 100 mg of ZrCl₄ was used instead of 80 mg of ZrS₂.

2.8. In-Situ Fabrication of Randomly Oriented NH₂-UiO-66 Membrane. ZrCl₄, NH₂-BDC, CH₃COOH, and DI water were dissolved in 60 mL of DMF under stirring to give a molar composition of Zr⁴⁺/NH₂-BDC/H₂O/AC/DMF = 1:1:1:150:500. Then, the precursor solution was poured into a Teflon-lined stainless-steel autoclave where the α -Al₂O₃ substrate was placed vertically. The membrane was obtained after solvothermal growth at 120 °C for 72 h. Finally, the membrane was rinsed with a copious amount of anhydrous methanol and dried for 12 h.

2.9. Characterizations. Phase purity and preferred orientation of NH₂-UiO-66 seeds and membranes were confirmed by Rigaku X-ray diffractometer with Cu-K α radiation at 40 kV and 100 mA. Scanning electron microscopy (SEM) images coupled with energy-dispersive X-ray spectrometry (EDXS) were performed on the FLEXSEM-1000 instrument.

2.10. Gas Permeation Test. The prepared NH₂-UiO-66 membrane was fixed in a module sealed with O-rings. Ar (50 mL·min^{−1}) was used as the sweep gas. For the mixed gas permeation test, both feed and sweep flow rates were set to 50 mL·min^{−1}, whereas the pressure at both sides was kept at 1 bar. A calibrated gas chromatograph (7890B, Agilent) was employed to measure the concentration of mixed gases on the permeate side. Separation factor (SF) $\alpha_{i/j}$ of a binary mixture is defined as the quotient of the molar ratio of components (*i, j*) in the permeate side divided by the quotient of the molar ratio of components (*i, j*) in the feed side

$$\alpha_{i/j} = \frac{\chi_{i,\text{perm}}/\chi_{j,\text{perm}}}{\chi_{i,\text{feed}}/\chi_{j,\text{feed}}}$$

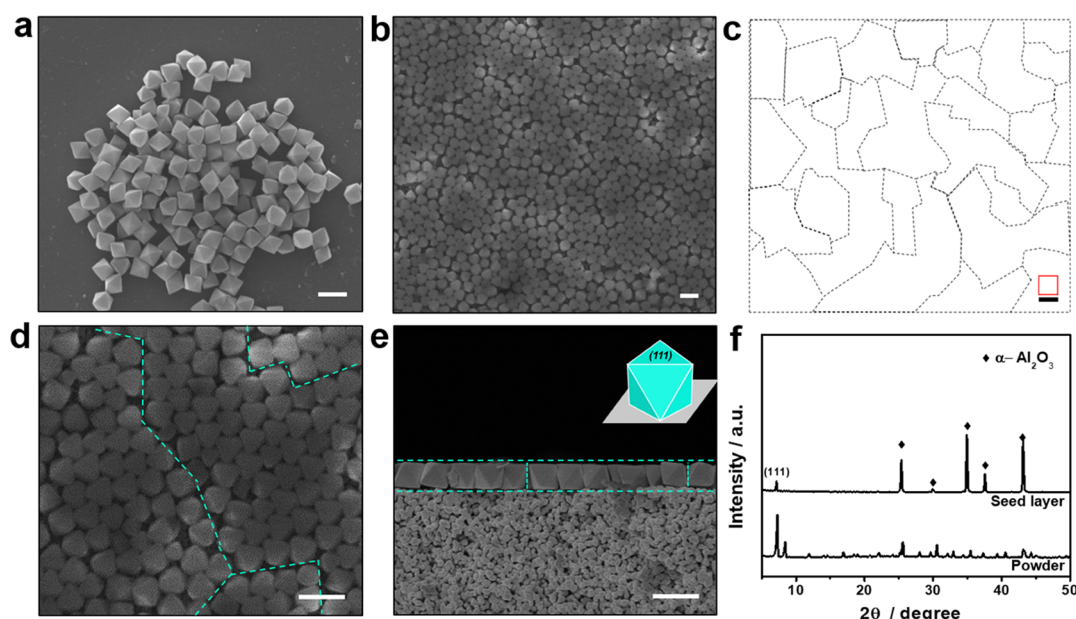


Figure 2. SEM images of (a) NH₂-UiO-66 seeds and (b) the prepared NH₂-UiO-66 seed layer. (c) Boundary images of oriented seed layer regions (red square represents the reference area of 1 μm² for 2500 pixel measured by photoshop, and the area of regions was calculated by the corresponding pixel divided by 2500). (d,e) Magnified top and cross-sectional views of the prepared NH₂-UiO-66 seed layer on the α-Al₂O₃ substrate. The scale bar is 1 μm. (f) Corresponding XRD patterns of the NH₂-UiO-66 seed powder and the seed layer.

3. RESULTS AND DISCUSSION

3.1. Preparation of Oriented NH₂-UiO-66 Seed Layer.

Initially, uniform octahedral-shaped NH₂-UiO-66 seeds with an average grain size of 600 nm were synthesized by a facile solvothermal method (shown in Figure 2a).³² Prior to oriented deposition, NH₂-UiO-66 seeds were vigorously stirred in the ethanol solvent containing trace amounts of PVP, until uniformly dispersed.

Consequently, a facile DALIAS method was employed for organizing NH₂-UiO-66 seeds into highly oriented seed layers on porous α-Al₂O₃ substrates (Figure S1). Prior to oriented deposition, a rectangular vessel connected with a circulating water pump was filled with DI water. Afterward, the seed suspension was gently injected on the turbulent water surface with a microsyringe until the final formation of a continuous and oriented NH₂-UiO-66 seed layer, which could be easily transferred on the porous α-Al₂O₃ substrate. As shown in Figure 2b, the prepared NH₂-UiO-66 seed monolayer was highly uniform and closely packed; moreover, NH₂-UiO-66 seeds tended to attach to the substrate surface with (111) facets as desired (Figure 2d,e). The dominance of preferred (111) out-of-plane orientation could be further confirmed by the X-ray diffraction (XRD) pattern (Figure 2f). Particularly, it was noted that the obtained seed monolayer could be further subdivided into several independent regions in which octahedral-shaped NH₂-UiO-66 seeds not only arranged in hexagonal planar arrays but also showed a high degree of in-plane orientation. The area of each independent region in Figure 2b was measured by dividing them into pixels (Figure 2c). Pixel-based image analysis indicated that the areas of these independent regions ranged between 4.0 and 24.8 μm², which corresponded to a 5–12 fold decrease in the anisotropic grain boundaries compared with identical grain-sized UiO-66 seed layers with a mere out-of-plane orientation by rough estimation. The capillary, hydrogen bonding, and van der Waals forces may jointly contribute to the regulation of the

preferred in-plane orientation.^{33,34} Indeed, only by adopting a closely packed hexagonal structure and an in-plane orientation could in-plane overlap areas be maximized, resulting in minimization of the total Gibbs free energy of the seed layer. The DALIAS method was considered as an ideal candidate for in-plane orientation control of MOF seed layers because the turbulent interface provided sufficient driving force to achieve closely packed structures, whereas the high mobility of MOF seeds floating at the air–liquid interface facilitated their in-plane self-assembly, resulting in the formation of a closely packed MOF seed monolayer maintaining regional in-plane orientation.

3.2. Fabrication of Oriented NH₂-UiO-66 Membrane.

The final step involved solvothermal epitaxial growth during which the prepared NH₂-UiO-66 membrane should preserve the preferred orientation inherited from the seed layer. Initially, zirconium chloride (ZrCl₄), which was commonly employed in Zr-MOF synthesis, was used as the zirconium source. Nevertheless, our results showed that not only substantial twin crystals were generated on the membrane surface but also prepared NH₂-UiO-66 membranes were still poorly intergrown, even though the solvothermal condition had been substantially optimized (Figure S2). The generation of undesired twins and insufficient seed intergrowth could be attributed to excessive nucleation and growth of NH₂-UiO-66 crystals in the bulk solution. Therefore, suppression of bulk nucleation of NH₂-UiO-66 crystals during the solvothermal epitaxial growth became necessary.

Our recent study indicated that layered TiS₂ as a representative of transition-metal dichalcogenides could serve as titanium precursors for the synthesis of qualified Ti-MOF crystals because of the layered structure and decent Ti–S bond strength.³⁵ Moreover, the slow and uniform dissolution rate of layered TiS₂ under solvothermal conditions resulted in effective suppression of bulk nucleation of NH₂-MIL-125(Ti) crystals so that the preferred *c*-orientation inherited from NH₂-MIL-125(Ti) seed layers was preserved during the epitaxial

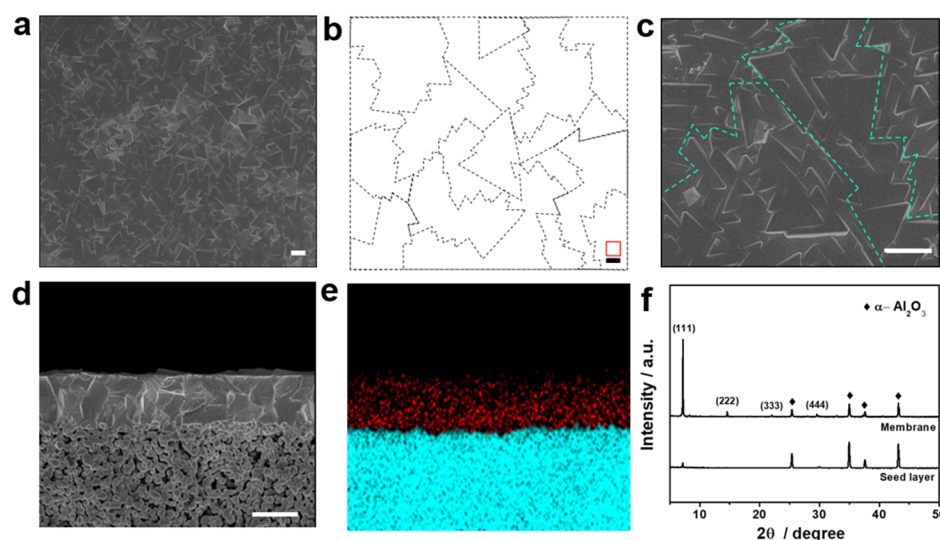


Figure 3. (a) SEM image of the oriented $\text{NH}_2\text{-UiO-66}$ membrane prepared under conventional heating with ZrS_2 as the metal source. (b) Boundary images of oriented regions (red square represents the reference area of $1\ \mu\text{m}^2$ for 2500 pixel measured by photoshop, and the area of regions was calculated by the corresponding pixel divided by 2500). (c,d) Magnified top and cross-sectional views of the prepared $\text{NH}_2\text{-UiO-66}$ seed layer on the $\alpha\text{-Al}_2\text{O}_3$ substrate. The scale bar is $1\ \mu\text{m}$. (e) Cross-sectional EDXS pattern of $\text{NH}_2\text{-UiO-66}$ membranes on $\alpha\text{-Al}_2\text{O}_3$ substrates (color code: red = Zr; cyan = Al). (f) Corresponding XRD patterns of the $\text{NH}_2\text{-UiO-66}$ membrane and the seed layer.

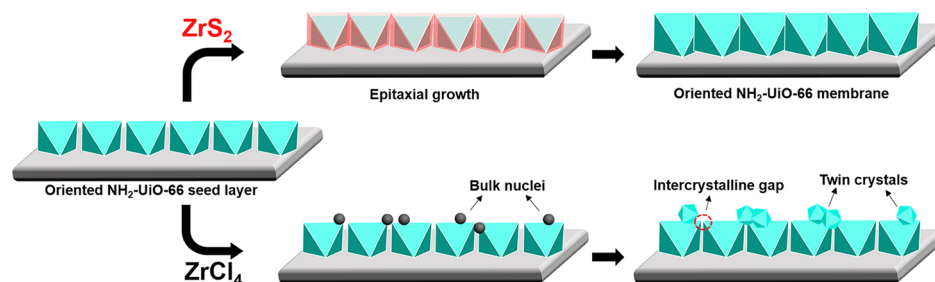


Figure 4. Schematic illustration of the proposed formation mechanism of $\text{NH}_2\text{-UiO-66}$ membrane-synthesized secondary growth using ZrS_2 and ZrCl_4 as metal sources.

growth. By analogy, in this study, it was hypothesized that layered ZrS_2 , which was chemically stable^{36,37} and prone to dissolve in the precursor solution gradually and homogeneously during the solvothermal epitaxial growth, may be competent in suppressing bulk nucleation and twin growth. Indeed, our results indicated that the use of layered ZrS_2 as zirconium precursors promoted the formation of a well-intergrown $\text{NH}_2\text{-UiO-66}$ membrane with few twins under optimized solvothermal conditions (Figure 3a–f). Cross-sectional image further indicated that the prepared $\text{NH}_2\text{-UiO-66}$ membranes were $\sim 1.2\ \mu\text{m}$ thick (Figure 3d). Besides, the existence of a sharp boundary in the cross-sectional EDXS pattern indicated that the $\text{NH}_2\text{-UiO-66}$ top layer did not penetrate deep into the porous substrate (Figure 3e). In addition, elemental analysis results further indicated that the sulfur element rarely existed in the membrane (Figure S3). The XRD pattern (Figure 3f) of the prepared $\text{NH}_2\text{-UiO-66}$ membrane exhibited two conspicuous diffraction peaks at 2θ values of 7.3 and 14.6° corresponding to (111) and (222) crystal planes, respectively, which unambiguously demonstrated the dominance of (111) out-of-plane orientation.

Notably, it was observed that the $\text{NH}_2\text{-UiO-66}$ membrane after epitaxial growth was composed of several independent regions where octahedral-shaped $\text{NH}_2\text{-UiO-66}$ grains exhibited a high degree of in-plane orientation. Furthermore, the area of

each independent region in Figure 3a was calculated, and the pixel-based image analysis (Figure 3b) indicated that areas of these independent regions ranged between 6.8 and $35.5\ \mu\text{m}^2$, implying that the regional in-plane orientation inherited from the seed layer was well preserved.

To fully elucidate the microstructural evolution mechanism of $\text{NH}_2\text{-UiO-66}$ membrane with layered ZrS_2 as the metal source, the influence of reaction time on the surface morphology of $\text{NH}_2\text{-UiO-66}$ membranes was further investigated (Figure S4). At the initial stage of epitaxial growth (3 h), a continuous and uniform epitaxial layer gradually formed on the surface of the $\text{NH}_2\text{-UiO-66}$ seed layer. $\text{NH}_2\text{-UiO-66}$ seeds continued to grow larger and began to merge with each other by further extending the synthesis time to 6 h. It was worth noticing there were no obvious twin crystals on the membrane surface during the whole growth period, which convincingly indicated that undesired bulk nucleation and twin growth had been effectively suppressed. A straightforward comparison of epitaxial growth mechanisms of $\text{NH}_2\text{-UiO-66}$ membranes prepared from ZrCl_4 and layered ZrS_2 precursors is schematically illustrated in Figure 4.

Our previous research indicated that microwave heating could serve as a powerful tool for the fast synthesis of twin-free highly oriented MOF membranes, relying on the unique thermal and nonthermal effects (like the nucleation-related

bottle-neck effect).³ In this study, single-mode microwave heating was further employed in the epitaxial growth of NH₂-UiO-66 membrane. Nevertheless, NH₂-UiO-66 seeds rarely grew up even under optimized synthetic conditions (Figure S5), implying that the precursor solution was incapable of adsorbing microwave irradiation efficiently probably due to the lower dielectric loss factor of the reaction medium ($\tan \delta_{\text{DMF}} = 0.161$).^{38–40} It was noted that recently, we prepared well-intergrown *c*-oriented NH₂-MIL-125(Ti) membranes by conducting single-mode microwave heating in a precursor solution containing a mixed DMF/MeOH (*v/v* = 1/1) solvent. Because the loss tangent value of methanol ($\tan \delta_{\text{MeOH}} = 0.659$) was higher than that of pure DMF, the microwave absorption efficiency was significantly enhanced, which led to the formation of NH₂-MIL-125(Ti) membranes with improved microstructures. Future research should be focused on developing facile methods for improving the microwave absorption efficiency of the reaction medium with low $\tan \delta$.

3.3. Separation Performance and Stability of NH₂-UiO-66 Membranes. Gas separation performance of the oriented NH₂-UiO-66 membrane was evaluated by measuring the volumetric flow rates of mixed gas pairs (Table 1). It was

Table 1. Permeability and SF of Binary Gas through the Oriented NH₂-UiO-66 Membrane at 20 °C and 1 Bar

gas mixture	H ₂ permeability (Barrers)	permeability (Barrers)	Knudsen selectivity	SF
H ₂ /CO ₂	1247.3	44.3 (CO ₂)	4.7	28.2
H ₂ /N ₂	1250.8	95.7 (N ₂)	3.7	13.1
H ₂ /CH ₄	1254.4	98.6 (CH ₄)	2.8	12.7

found that the SF of H₂/CO₂, H₂/N₂, and H₂/CH₄ gas pairs reached 28.2, 13.1, and 12.7, respectively, which was far above the corresponding Knudsen selectivity. The much higher H₂/CO₂ selectivity compared with H₂/N₂ and H₂/CH₄ gas pairs could be ascribed to preferential adsorption of CO₂ within the NH₂-UiO-66 framework, resulting in significant reduction in CO₂ diffusion coefficient and CO₂ permeability. In particular, the SF of the H₂/CO₂ binary gas mixture was not only obviously higher than that of other pure UiO-66-series membranes under similar test conditions but also far exceeded the 2008 Robeson upper-bound line (Figure 5a). In contrast, both SF of the H₂/CO₂ gas pair and H₂ permeability of the randomly oriented 4 μm -thick NH₂-UiO-66 membrane prepared by facile in situ solvothermal growth (Figure S6 and Table S1)⁴² were remarkably lower than those of the

oriented NH₂-UiO-66 membrane, which vividly demonstrated the importance of preferred orientation control in the performance enhancement of MOF membranes.

Recently, we prepared *c*-oriented 0.5 μm -thick NH₂-MIL-125(Ti) membranes on porous α -Al₂O₃ substrates showing significantly lower H₂ permeability as well as H₂/CO₂ selectivity in comparison with oriented NH₂-UiO-66 membranes, even though their grain size, pore aperture, and functionality were quite similar.⁴³ The enhanced separation performance of the prepared NH₂-UiO-66 membranes could at least partially be attributed to the regional in-plane orientation, which reduced the grain boundary defects and the diffusion barrier further. Nevertheless, a more in-depth investigation of the positive effect of in-plane orientation on the separation performance of MOF membranes was still required to fully identify the structure-performance relationship.

The influence of operating temperature on the H₂/CO₂ separation performance of both oriented and randomly oriented NH₂-UiO-66 membranes was further investigated. It was found that their H₂ permeability and the SF of the H₂/CO₂ gas pair strongly depended on the operating temperature (shown in Figures S7 and S8). Upon increasing the temperature from 20 to 120 °C, the H₂ permeability steadily increased, whereas the SF of the H₂/CO₂ gas pair was slightly decreased, which was due to a weakened affinity between CO₂ molecules and –NH₂ functional groups within the NH₂-UiO-66 framework.^{44–47} In addition, enhanced framework flexibility with temperature may partially contribute to the decreased H₂/CO₂ SF either.^{24,48,49}

Both oriented and randomly oriented NH₂-UiO-66 membranes further showed long-term stability. Our research indicated that their H₂ permeability and the SF of the H₂/CO₂ gas pair remained unchanged within 50 h (shown in Figures Sb and S9). In addition, the mechanical stability of the prepared NH₂-UiO-66 membranes was evaluated. It was observed that there remained few cracks on the surface of the oriented NH₂-UiO-66 membrane after strong sonication for 60 min in DI water, which indicated well-intergrowth between adjacent crystals and firm attachment of the NH₂-UiO-66 membrane to the substrate surface. In contrast, substantial cracks were generated, and noticeable detachment of NH₂-UiO-66 grains from the substrate surface occurred on the randomly oriented NH₂-UiO-66 membrane under identical test conditions (Figure S10). The excellent H₂/CO₂ separation performance, long-term operation stability, and mechanical stability suggested that the oriented NH₂-UiO-66 membranes were

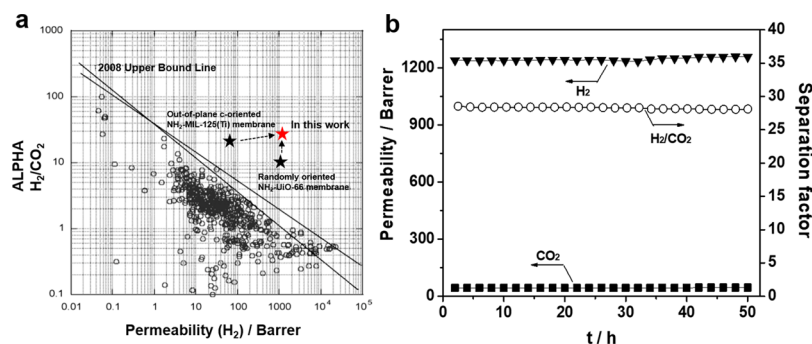


Figure 5. (a) Comparison of H₂/CO₂ separation performance of oriented NH₂-UiO-66 membrane with randomly oriented NH₂-UiO-66 membrane and out-of-plane *c*-oriented NH₂-MIL-125(Ti) membrane. The 2008 Robeson upper bound line for H₂/CO₂ separation is cited from ref 41. (b) Long-term stability of the oriented NH₂-UiO-66 membrane at 20 °C and 1 bar.

promising candidates for efficient H₂ purification and CO₂ capture.

4. CONCLUSIONS

In conclusion, in this study, well-intergrown NH₂-UiO-66 membranes with both (111) out-of-plane and regional in-plane orientations were prepared by conducting the oriented epitaxial growth method. DALIAS method was applied for self-assembly of uniform octahedral-shaped NH₂-UiO-66 seeds into closely packed NH₂-UiO-66 seed monolayers with both (111) out-of-plane and regional in-plane orientations, whereas the employment of layered ZrS₂ as the metal precursor was found indispensable for sealing intercrystalline gaps while preserving orientations inherited from seed layers. The prepared NH₂-UiO-66 membrane exhibited superior H₂/CO₂ selectivity and considerable H₂ permeance compared to their counterparts with random and/or mere out-of-plane orientations as well as NH₂-MIL-125(Ti) membranes with a mere out-of-plane orientation. It is expected that the concept of in-plane orientation control could be illustrative for the separation performance enhancement of diverse molecular sieve membranes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.9b18804>.

Schematic illustration of dynamic air-liquid interface-assisted self-assembly, secondary growth of NH₂-UiO-66 membrane under conventional heating with ZrCl₄ as the metal source, elemental composition of the prepared oriented NH₂-UiO-66 membrane, microstructural evolution process of the oriented NH₂-UiO-66 membrane, secondary growth of NH₂-UiO-66 membrane under single-mode microwave heating with ZrS₂ as the metal source, randomly oriented NH₂-UiO-66 membrane prepared by in-situ crystallization, gas separation performance of the randomly oriented NH₂-UiO-66 membrane, investigation of the effect of operating temperature on the separation performance of the prepared oriented NH₂-UiO-66 membrane and the randomly oriented NH₂-UiO-66 membrane, long-term stability of the randomly oriented NH₂-UiO-66 membrane, and investigation of the adhesion strength of NH₂-UiO-66 membranes (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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