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Fabrication of highly CO_2/N_2 selective polycrystalline UiO-66 membrane with two-dimensional transition metal dichalcogenides as zirconium source via tertiary solvothermal growth

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Keywords: Metal-organic frameworks	Zirconium-based MOF (Zr-MOF) membranes have attracted widespread attention due to their highly tailorable
UiO-66 Membranes	defect regulation as well as extraordinary chemical thermal stability. Nevertheless, it has remained a great
Transition metal dichalcogenides Gas separation	zirconium sources and heating modes. In this study, we prepared polycrystalline UiO-66 membranes exhibiting

1. Introduction

In recent decades, zirconium-based metal-organic framework (Zr-MOF) membranes have shown promising performance in terms of gas separation [1-9], pervaporation [7,10-12], desalination [1] and nanofiltration [8]. Among them, UiO-66-type MOF membranes, which possessed the chemical formula $Zr_6O_4(OH)_4(BDC)_6$ (BDC = 1,4-benzenedicarboxylic acid) as well as the *fcu*-type topology, have been extensively studied due to their appropriate pore size and tunable adsorption group behavior caused bv functional decoration or ligand/cluster-missing defect regulation [1,8,13]. In addition, they exhibited extraordinary chemical and thermal stability under harsh operating conditions [8,13]. Liu et al. pioneered the fabrication of porous α -Al₂O₃ hollow fiber-supported continuous polycrystalline UiO-66 membranes via a facile in situ solvothermal process [1]. Prepared membranes exhibited excellent multivalent ion rejection, making them highly promising for desalination and water treatment. Since then, related research has flourished in exploring their potential applications concerning membrane-based separation [8]. Polycrystalline UiO-66 membranes also displayed bright prospects in pervaporation dehydration of organics [10] and desulfurization [12]. Besides being in a

polycrystalline form, diverse UiO-66-based mixed matrix membranes were also fabricated and showed attractive separation performances [14-17]. It should be noted that despite of great efforts that have been made, most researches have been devoted to improving their liquid separation performance [8]. In contrast, so far only limited attention has been paid to enhancing their gas separation performance, although UiO-66 membranes should exhibit higher CO2/N2 separation performance due to the high affinity interactions between CO₂ and hydroxvlated Zr₆ cluster in the UiO-66 framework [8]. This phenomenon could be partially ascribed to quite limited innovation in zirconium source and fabrication process. For instance, ZrCl₄ has been commonly used zirconium source of UiO-66 membranes [1-3]. Nevertheless, ZrCl₄ was extremely vulnerable to hydrolysis even upon transient exposure to trace amount of water, therefore making it impossible to accurately control nucleation and growth kinetics of UiO-66 crystals on porous substrates under solvothermal reaction conditions. It is therefore anticipated that the use of more water-stable zirconium source instead may contribute to microstructural optimization and performance enhancement of UiO-66 membranes.

unprecedented CO_2/N_2 selectivity (31.3). The use of layered ZrS_2 , a representative of transition-metal dichalcogenides (TMDCs), as zirconium source during tertiary solvothermal growth was found to be indispensable for improving the separation performance of UiO-66 membranes. As far as we know, the CO_2/N_2 selectivity reported in this study was the highest among all pristine polycrystalline MOF membranes measured under ambient conditions. More importantly, our study highlighted the importance of concurrent metal source and fabrication

process innovation in performance enhancement of polycrystalline MOF membranes.

In the present work, UiO-66 membranes with superior CO_2/N_2 separation performance were obtained through concurrent zirconium

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source and fabrication process innovation (schematically shown in Fig. 1). On the one hand, layered ZrS₂, a representative of TMDCs which had shown potential applications in field-effect transistors (FETs) [18], gas sensors [19] and field-emission battery [20,21], was employed as zirconium source during the solvothermal growth of UiO-66 membranes. Owing to its higher chemical and water stability, the dissolution rate of layered ZrS2 in the precursor solution was observably slower, which was potentially beneficial to suppression of homogenous UiO-66 crystal nucleation and growth in the bulk solution; moreover, the undesired adverse reaction which may be caused by decomposition of zirconium source in the presence of even trace amount of water could be effectively avoided; on the other hand, tertiary solvothermal growth was conducted and proved essential for reducing grain boundary defects. UiO-66 membranes prepared in this way showed superb ideal selectivity towards the CO₂/N₂ gas pair (31.3) which, represented the highest value among all pristine polycrystalline MOF membranes measured under ambient conditions [1,5,22-37].

2. Experimental section

2.1. Materials

Zirconium tetrachloride (ZrCl₄, 99.5%, Aladdin), zirconium disulfide (ZrS₂, 99.5%, Alfa Aesar), N,N-dimethylformamide (DMF, 99.8%, Kemiou), methanol (CH₄O, 99.5%, Macklin), 1,4-benzenedicarboxylic acid (BDC, 99%, Aladdin) and acetic acid (HAc, 99.5%, Kemiou) were used as received. Porous α -Al₂O₃ disks with the pore size of 70 nm and diameter of 18 nm were purchased from Fraunhofer IKTS, Germany.

2.2. Synthesis of UiO-66 powders using layered ZrS_2 as metal source

Layered ZrS₂ and H₂BDC were dissolved in a DMF-HAc mixed solvent with a molar ratio of ZrS₂/H₂BDC/HAc/DMF = 1:1.15:100:500 under vigorously stirring for 20 min. Consequently, the precursor solution was heated in an oven at 140 °C for 96 h. After cooling down, the solid products were centrifuged, washed with DMF and ethanol three times, and finally dried overnight under vacuum.

2.3. Synthesis of UiO-66 seeds and seed layer deposition

First of all, regular UiO-66 seeds were prepared following the previous report [38]. Briefly, $ZrCl_4$ and H_2BDC were dissolved in a DMF-HAc mixed solvent with a molar ratio of $ZrCl_4/H_2BDC/HAc/DMF$ = 1:1:160:800 under vigorous stirring. Prepared clear precursor solution was then poured into a 100 ml Teflon-lined autoclave and heated in an oven at 120 °C for 24 h. After that, the autoclave was cooled to room temperature. The white solid products were centrifuged, washed with DMF and methanol three times, and finally dried in a vacuum oven at 100 °C overnight. It's worth noting that all utensils must be thoroughly dried before use since even trace amount of water may severely influence on the morphology of UiO-66 seeds.

The UiO-66 seed suspension was obtained via first dispersing 0.021 g UiO-66 seeds into 7 g methanol by sonication for 30 min. Consequently, the seed suspension was deposited on the porous α -Al₂O₃ substrate by spin-coating at 4000 rpm for 60 s. Finally, the substrate coated with UiO-66 seed layer was dried at 70 °C for 6 h before use.

2.4. Secondary growth of UiO-66 membrane

Secondary growth of UiO-66 membrane was carried out as follow: First, layered ZrS₂ and H₂BDC were dissolved in a DMF-HAc mixed solvent with a molar ratio of ZrS₂/H₂BDC/HAc/DMF = 1:1.15:100:500 to form the precursor solution. Consequently, the substrate coated by the UiO-66 seed layer was vertically placed into a 50 ml Teflon-lined stainless-steel autoclave with a Teflon holder. In the next step, the precursor solution was added into the vessel and treated in a preheated convective oven at 140 °C for 48 h. After crystallization, the membrane was taken out and gently washed with methanol. Finally, the membrane was dried at 25 °C for 12 h under vacuum.

2.5. Tertiary growth of UiO-66 membrane

To reduced grain boundary defects, tertiary growth was further carried out right after the completion of secondary growth. The procedure for tertiary growth was similar to section 2.4 except that the reaction time was reduced to 24 h.

2.6. Synthesis of UiO-66 membrane by in situ growth

As a comparative experiment, we further tried to prepare UiO-66 membrane via facile *in situ* solvothermal method. First, a certain amount of H₂BDC was dissolved in 30 ml DMF with a molar ratio of BDC/DMF = 1:500 under vigorous stirring. Consequently, a bare porous α -Al₂O₃ substrate was dip-coated in the precursor solution for three times and dried at 70 °C for 3 h prior to use. Finally, solvothermal *in situ* growth was carried out in accordance with the procedure described in



Fig. 1. Schematic illustration of preparation of UiO-66 membrane using layered ZrS₂ as zirconium source by tertiary growth. Framework structures of layered ZrS₂ and UiO-66 are derived from Ref. [3,14], respectively.

section 2.4.

2.7. Secondary growth of UiO-66 membrane by single-mode microwaveassisted synthesis

The composition of precursor solution for the single-mode microwave-assisted secondary growth was similar to section 2.4. Then 30 ml solution was transferred into a 80 ml glass vessel where the UiO-66 seeded substrate was vertically placed. Afterwards, the vessel was sealed and secondary growth was conducted in a single-mode microwave oven (Discover, CEM) at 140 $^{\circ}$ C for 60 min.

2.8. Characterization details

Scanning Electron Microscope (SEM) images were obtained with a FlexSEM 1000 SEM at an accelerating voltage 10 kV and 15 kV, respectively. X-ray diffraction (XRD) patterns of powders, seed layers and membranes were recorded by a Rigaku SmartLab diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm) at a scanning rate of 8°/min in the rage of 5–50°. Thermogravimetric analysis (TGA) was recorded on a NETZSCH (TG 209) thermal analyzer in nitrogen atmosphere from 40 to 800 °C at a ramping rate of 10 °C·min⁻¹.

Gas separation performance was measured under ambient conditions. The concentration of gases was obtained through a gas chromatograph (7890B GC, Agilent). The flow rate for each gas in the feed gas was set at 50 ml min⁻¹. Helium (50 ml min⁻¹) was served as sweep gas. Ideal selectivity was calculated by the quotient of the permeance of gas A and gas B in the permeate side. Separation factor (SF) $\alpha_{A/B}$ of mixed gases could be expressed as follow:

$$\alpha_{A/B} = \frac{y_A/y_B}{x_A/x_B}$$

y and *x* represented volumetric fractions of each component in the permeate side and feed side, respectively.

3. Results and discussion

3.1. Preparation of UiO-66 powders with layered ZrS_2 as zirconium source

Herein we first verified the feasibility of the preparation of UiO-66 powders via solvothermal treatment of the layered ZrS_2 precursor. Our results indicated that octahedral-shaped UiO-66 crystals could be prepared via facile solvothermal treatment of layered ZrS_2 with H₂BDC ligands (Fig. 2a). The XRD pattern (Fig. 2b) further indicated that all diffraction peaks matched well with the standard pattern of UiO-66 phase [13]. Moreover, the sharp and strong diffraction peaks implied

that prepared UiO-66 powders had good crystallinity. It should be noted that being analogous to other common zirconium sources (like ZrCl₄), addition of given amount of acids (like acetic acid) in the precursor solution was necessary to maintain a relatively high crystallinity since it was observed that layered ZrS2 could hardly be transformed to UiO-66 crystals in the absence of HAc under identical reaction conditions (shown in Fig. S1). It has been well documented that monocarboxylic acids, which commonly served as the modulator during Zr-MOF synthesis, enabled to enhance the crystallinity or tailor the crystal morphology through "deprotonation modulation" (i.e., deprotonation of the linker molecules) or "coordination modulation" (i.e., competition between monocarboxylic acids and linker molecules for the coordination sites at Zrn clusters) [22,38-46]. Previous studies indicated that "coordination modulation" took a dominant role in the presence of HAc during solvothermal synthesis of UiO-66 crystals, yielding highly defective structures [22,41]. In effect, structural defects including "missing linker" and "missing cluster" in UiO-66 powders had been directly observed by Liu et al. with HRTEM [39]. Although the relationship between UiO-66 membrane separation performance and structural defects present in the framework remained controversial, there was no doubt that the presence of structural defects exerted significant influence on their pore size, pore volume, gas uptake capacity and selective adsorption behavior [39,41-43]. For instance, Liang et al. indicated that the existence of structural defects had a pronounced effect on CO2 adsorption behavior of UiO-66 powders [47]; moreover, Wu et al. demonstrated that the addition of HAc into the precursor solution significantly facilitated the introduction of defects and mesopores within Zr-MOF particles, resulting in a significant increase in pore volume, surface area and CO_2 uptake [22]. Since the separation of CO_2/N_2 gas pair mainly relied on preferential adsorption of CO₂ molecules at the unsaturated coordination sites rather than size-based molecular sieving, we assumed that the presence of structural defects may facilitate the preferential CO2 adsorption and therefore, the enhancement of CO2/N2 selectivity.

In addition to the phase purity and surface morphology, thermal stability of layered ZrS₂-derived UiO-66 powders was further evaluated by TGA analysis. Our experimental results indicated that like those prepared from common zirconium sources like ZrCl₄, layered ZrS₂-derived UiO-66 powders were thermally stable up to ~500 °C (shown in Fig. 3), thereby showing great promise for long-term operation under harsh conditions.

3.2. Secondary growth of UiO-66 membrane

Initially, we tried to prepare continuous UiO-66 membrane on bare porous α -Al₂O₃ substrate with layered ZrS₂ as zirconium source by means of *in situ* solvothermal growth. Nevertheless, it turned out to be



Fig. 2. a) SEM image of UiO-66 powders prepared by solvothermal synthesis using layered ZrS₂ as zirconium source; b) XRD patterns of simulated UiO-66, layered ZrS₂ precursor and prepared UiO-66 powders.



Fig. 3. TGA curves of UiO-66 powders prepared by acetic acid-modulated solvothermal synthesis using $ZrCl_4$ and layered ZrS_2 as zirconium sources, respectively.

extremely difficult to completely seal grain boundary defects even under the optimal reaction conditions (Fig. 4a and b). This could be attributed to low affinity interactions between porous α -Al₂O₃ substrate surface and UiO-66 powders. Although surface modification of the substrate with ligands prior to *in situ* solvothermal growth gave rise to considerable increase in heterogeneous nucleation density, grain boundary defects between neighboring UiO-66 crystallites remained clearly visible (Fig. 4c and d). To increase the nucleation density of UiO-66 crystallites on the substrate surface, instead of *in situ* solvothermal growth, herein solvothermal epitaxial growth was involved in UiO-66 membrane preparation.

The first step involved the preparation of nano-sized UiO-66 seeds.

The seeds obtained via simple solvothermal synthesis showed uniform octahedral shape with an average size of 500 nm (Fig. 5a and Fig. 6a). Consequently, spin-coating was employed for uniform deposition of the UiO-66 seed layer on the α -Al₂O₃ support surface. After spin-coating under controlled conditions, a closely packed seed layer was obtained (shown in Fig. 5b and Fig. S2). The cross-section SEM image indicated that thickness of the seed layer was $\sim 1 \,\mu m$, which roughly equaled to twice that of a UiO-66 monolayer. In the next step, secondary growth was carried out to seal grain boundary gaps (Fig. S3 and Fig. S4). As confirmed by SEM images, prepared UiO-66 membrane was wellintergrown with an average grain size of 1.2 μ m, and there were no visible pinholes, cracks or other defects on the substrate surface (Fig. 5c). Cross-sectional image confirmed that thickness of prepared UiO-66 membrane reached 1.6 µm (Fig. 5d). Corresponding XRD patterns further demonstrated that obtained membrane indeed belonged to pure UiO-66 phase with no preferred orientation (Fig. 6b and c).

Finally, gas permeation tests were conducted to evaluate the separation performance of prepared UiO-66 membrane. Results of single gas permeation experiments indicated that compared with other gases (i.e., H_2 , N_2 and CH_4), CO_2 preferentially permeated through the UiO-66 membrane and the ideal selectivity of CO_2/N_2 , H_2/N_2 , and CO_2/CH_4 gas pairs reached 9.4, 6.4 and 6.1 (shown in Fig. 7), respectively, which illustrated that molecular sieving mechanism played a dominant role in the gas permeation process. Nevertheless, these values remained lower than those reported in previous literature, which demonstrated that substantial grain boundary defects still existed which, as shown below, inspired us to fix these defects by conducting tertiary solvothermal growth.

3.3. Tertiary growth of UiO-66 membrane

UiO-66 membrane obtained after tertiary solvothermal growth remained well-intergrown and highly uniform. Moreover, as shown in SEM images, the grain size of prepared UiO-66 membrane became larger (Fig. 8a) and membrane thickness was increased to $3.5 \,\mu$ m (Fig. 8b). In addition, it was noticed that the grain size of prepared UiO-66



Fig. 4. SEM images of UiO-66 membranes prepared by *in situ* solvothermal growth with layered ZrS_2 as zirconium source on a, b) bare porous α -Al₂O₃ substrate and c, d) ligand-modified substrate.



Fig. 5. SEM images of a) UiO-66 seeds; b) top and cross-sectional views of prepared UiO-66 seed layer on the α -Al₂O₃ substrate; c, d) top and cross-sectional views of prepared UiO-66 membrane by secondary growth with layered ZrS₂ as zirconium source.



Fig. 6. XRD patterns of a) UiO-66 seeds; b) UiO-66 seed layer on porous α -Al₂O₃ substrate and UiO-66 membrane synthesized by c) secondary growth and d) tertiary growth. Note: * indicated diffraction peaks derived from porous α -Al₂O₃ substrate.

membrane was not uniform, which could be attributed to Ostwald Ripening mechanism or random surface attachment of UiO-66 crystals nucleated in bulk solution on the substrate. XRD patterns indicated that prepared membrane still belonged to pure UiO-66 phase (Fig. 6d). Obviously, concurrent increase in grain size and membrane thickness was potentially beneficial for further reducing grain boundary defects and improving the separation performance of prepared UiO-66 membrane.

Single gas permeation behavior of the UiO-66 membrane obtained

after tertiary solvothermal growth implied that CO₂ permeance remained much higher than all other gases (Fig. 9a). In particular, ideal selectivity of the CO₂/N₂ gas pair sharply rose to 31.3, which represented the highest value among all pristine polycrystalline MOF membranes measured under ambient conditions as reported in the literature (Table 1). In addition, mixed gas separation performance of UiO-66 membrane was further measured (Table S2) and separation factor (SF) of equimolar CO₂/N₂, H₂/N₂, CO₂/CH₄ and H₂/CH₄ gas pairs reached 21.4, 13.9, 9.3 and 6.4, respectively (shown in Fig. 9b). It was noted that although being slightly lower than their corresponding ideal selectivity, SF of CO₂/N₂ mixture remained superior to that of other crystalline MOF membranes measured under ambient conditions (Table 1). It should be particularly noted that polycrystalline MOF-5 membranes prepared by Lin et al. displayed superb CO₂/N₂ selectivity (410) at feed pressure of 505 kPa [37]; very recently Jiang and Li et al. reported the preparation of ZIF-62 glass MOF membranes with superior CO₂/N₂ selectivity (34.5) due to elimination of intercrystalline defects [36]. These findings suggested that there remained huge potential for CO2/N2 separation performance enhancement of MOF membranes.

It is well recognized that the membrane selectivity $(S_{mem(i/j)})$ can be well described by the interplay of adsorption selectivity $(S_{ads(i/i)})$ and diffusion selectivity ($S_{diff(i/j)}$) according to the following equation: S_{mem} $(i/i) = S_{ads(i/i)} \times S_{diff(i/i)}$ [48]. The reason why the CO₂/H₂ ideal selectivity is relatively low (~2) can be interpreted as follow: On the one hand, owing to the preferential adsorption between CO2 and hydroxylated Zr₆ cluster in the UiO-66 framework, prepared UiO-66 membrane should exhibit considerably high $S_{ads(CO2/H2)}$ (\gg 1); on the other hand, since the kinetic diameter of H_2 (2.9 Å) is smaller than that of CO_2 (3.3 Å), the diffusion coefficient of CO_2 in the UiO-66 framework should be lower than H₂, leading to lower $S_{diff(CO2/H2)}$ («1). As a result, the CO₂/H₂ ideal selectivity ($S_{\text{mem}(\text{CO2/H2})}$) is relatively low (~2). While the reason why the H₂/N₂ ideal selectivity is high (18.1) can be interpreted as follow: Since there is no adsorption interaction with the UiO-66 framework for both N2 and H2, as a result, prepared UiO-66 membrane should exhibit no adsorption selectivity, i.e., $S_{ads(H2/N2)} \approx 1$. In contrast, since the kinetic diameter of H_2 (2.9 Å) is smaller than that of



Fig. 7. a) Single-gas permeation behavior of UiO-66 membrane after secondary growth; b) ideal selectivity and SF of equimolar H_2/CH_4 , H_2/N_2 , CO_2/CH_4 and CO_2/N_2 gas pairs of corresponding UiO-66 membrane. Gas permeation test was carried out under ambient conditions.



Fig. 8. SEM images of a) top and b) cross-sectional views of prepared UiO-66 membrane after tertiary solvothermal growth with layered ZrS₂ as zirconium source.



Fig. 9. a) Single-gas permeation behavior of UiO-66 membrane prepared by tertiary growth; b) ideal selectivity and SF of equimolar H_2/CH_4 , H_2/N_2 , CO_2/CH_4 and CO_2/N_2 mixtures of prepared UiO-66 membrane. Gas permeation test was carried out under ambient conditions.

N₂ (3.64 Å), the diffusion coefficient of H₂ in the UiO-66 framework should be remarkably higher than H₂, leading to higher $S_{\text{diff}(\text{H}2/\text{N}2)}$ (\gg 1). As a result, the H₂/N₂ ideal selectivity, i.e., $S_{\text{mem}(\text{H}2/\text{N}2)}$, is comparatively high (18.1).

Consequently, long-term stability test was carried out and our experimental results indicated no discernible degradation of both CO_2 permeance and SF of the CO_2/N_2 gas pair within 24 h under ambient operating conditions (as shown in Fig. 10). Finally, mechanical stability of prepared UiO-66 membrane was determined by sonication in DI water for 1 h. As observed in Fig. S6, even after strong sonication, prepared UiO-66 membrane remained continuous and no discernible defects at the UiO-66 membrane-substrate interface could be observed, therefore

implying UiO-66 crystallites were firmed attached to the substrate surface. To sum up, our experimental results indicated that UiO-66 membranes were attractive for CO_2/N_2 separation relying on the excellent gas separation performance, high mechanical stability and reliable long-term operational stability.

3.4. Discussion on the necessity for combining layered ZrS_2 precursor with tertiary growth

Our previous research demonstrated that TMDCs could act as qualified metal source of diverse MOF membranes due to their unique 2D layered structure, high water/chemical stability and decent M-X

Table 1

Comparison of CO_2/N_2 gas separation performance between UiO-66 membrane prepared in this study and pristine polycrystalline MOF membranes reported in the literature. All gas permeation tests were conducted under ambient conditions.

Membrane	CO_2 Permeance (10 ⁻⁹ mol m ⁻² s ⁻² Pa ⁻¹)	CO ₂ /N ₂	CO ₂ /N ₂	
		Ideal Selectivity	SF (v/v = 1/1)	
ZIF-8/ZnO	39	1.95	-	[19]
ZIF-8	45	-	3.0	[20]
ZIF-8	34	2.4	-	[21]
ZIF-69	103	2.2	6.3	[22]
SIM-1	35	1.1	-	[23]
ZIF-7	0.76	-	13.6	[24]
CAU-1	730	14.8	-	[25]
CAU-1	1320	26.2	20.5	[26]
MIL-100	900	3.75	-	[27]
MMOF	70	1	-	[28]
Sod-ZMOF-	0.63	8.7	-	[29]
1				
Cu ₃ (BTC) ₂	281	1	-	[30]
Co/Zn-ZIF-	8.19	17.8	18.4	[31]
L				
UiO-66	580	26.5	-	[5]
UiO-66	950	29.7	-	[1]
UiO-66	37.6	31.3	21.4	This
				work



Fig. 10. a) Long-term stability of CO_2/N_2 gas separation performance of UiO-66 membrane after tertiary growth under ambient conditions.

bonding strength resulting in not only effective suppression of the adverse reaction (i.e., hydrolysis) but also better control over the release rate of metal species and therefore, the nucleation and growth rate of MOF membranes during the epitaxial growth [4,49,50]. For instance, in a recent study we prepared (111)-oriented NH₂-UiO-66 membranes exhibiting superior H₂/CO₂ selectivity [4] with layered ZrS₂ as zirconium source. It is, therefore, reasonable to assume that employing layered ZrS₂ as zirconium source also enabled effective reduction in grain boundary defects. Combining with tertiary solvothermal growth warranting better intergrowth between neighboring crystallites, our UiO-66 membrane exhibited superior CO_2/N_2 separation performance compared with all other pristine polycrystalline MOF membranes measured under ambient conditions.

Our previous study indicated that single-mode microwave heating could serve as a powerful tool for microstructural optimization and separation performance enhancement of diverse molecular sieve membranes [4,49,51–53]. In this work, we also tried to prepare UiO-66 membranes with layered ZrS_2 as zirconium source through

single-mode microwave heating. Nevertheless, it turned out to be very difficult to convert layered ZrS_2 precursor to UiO-66 membrane in the case of *in situ* and secondary growth possibly due to higher chemical stability of layered ZrS_2 precursor as well as lower dielectric loss factor of the reaction medium (Fig. S5). To summarize, although the use of TMDCs as metal source had proven to be an effective approach for enhancing separation performance of MOF membranes, the selection of an appropriate fabrication technique (e.g., tertiary solvothermal growth in this study) remained necessary to maximize their utility.

4. Conclusions

To summarize, in this work we successfully prepared highly CO₂/N₂ selective UiO-66 membranes on porous α-Al₂O₃ substrates by combining layered ZrS₂ as zirconium source with tertiary solvothermal growth. On the one hand, the use of layered ZrS₂ precursor not only effectively avoided undesired side reaction (i.e., hydrolysis) but also enabled better control over the release rate of zirconium species and growth rate of UiO-66 membrane during the epitaxial growth; on the other hand, employing tertiary growth warranted further reduction in grain boundary defects. As a result, prepared UiO-66 membrane exhibited higher CO₂/N₂ selectivity (31.3) compared with other pristine polycrystalline MOF membranes measured under ambient conditions. Our study indicated that unceasing innovation on metal source and fabrication process remained a powerful tool for improving separation performance of polycrystalline MOF membranes. Future study should be conducted on improving the CO2 permeance of UiO-66 membranes without significantly compromising the CO₂/N₂ selectivity.

Declaration of competing interest

The authors declare no competing financial interest.

CRediT authorship contribution statement

Rong Rong: Formal analysis, Data curation, Writing - original draft. **Yanwei Sun:** Visualization, Writing - review & editing. **Taotao Ji:** Formal analysis, Data curation. **Yi Liu:** Writing - original draft.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2020.118275.

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