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Fabrication of Defect-Engineered MOF-801 Membrane for Efficient Dye Rejection

Fuyuan Yan,^[a] Jiahui Yan,^[a] Yanwei Sun,^[a] Taotao Ji,^[a] Yongfu He,^[a] Xinwen Guo,^{*[a]} and Yi Liu^{*[a, b]}

Although having shown great promise for efficient water treatment, rational structural design and engineering of polycrystalline MOF membranes remain rarely investigated so far. In this study, we prepared well-intergrown MOF-801 membranes with tailorable structural deficiencies in the framework for application in dye rejection. Of particular note, we found that the addition of formic acid as modulator led to the formation of

Introduction

Polycrystalline Metal-organic framework (MOF) membranes have shown promising application in efficient gas and liquid separation due to their tailorable framework structure.^[1-2] high surface areas,^[3] and rich functionality.^[4] To date, hundreds of different types of MOF membranes have been fabricated and demonstrated attractive performances in gas separation (such as H₂ purification,^[5] CO₂ capture^[6] and olefin separation^[7]) and in liquid separation (such as dye rejection, $^{\scriptscriptstyle [8-20]}$ ion screening, $^{\scriptscriptstyle [21]}$ and pervaporation).^[22-24] In terms of water treatment, MOFpolymer composite membranes have been widely studied for ion screening and dye rejection. For instance, Wang et al. developed a novel LBL method to fabricate ZIF-8/PA membranes exhibiting high water flux (27.1 kg m⁻²h⁻¹) and rejection rate (99.8%).^[25] Bart Van der Bruggen. et al. applied two loose TFC NF membranes (Sepro NF 2 A and 6) to separate salts from dye/brine mixtures, achieving NaCl rejection rates over 95%.[21] Nevertheless, to date there remain few studies on exploring the potential applications of polycrystalline MOFs membranes in water treatment.

[a] F. Yan, J. Yan, Dr. Y. Sun, T. Ji, Y. He, Prof. X. Guo, Prof. Y. Liu State Key Laboratory of Fine Chemicals Frontiers Science Center for Smart Materials School of Chemical Engineering Dalian University of Technology Linggong Road NO. 2, Ganjingzi District Dalian 116024 (P. R. China) E-mail: guoxw@dlut.edu.cn diligenliu@dlut.edu.cn
[b] Prof. Y. Liu Dalian Key Laboratory of Membrane Materials and Membrane Processes Dalian University of Technology Linggong Road NO. 2, Ganjingzi District

- Dalian 116024 (P. R. China)
- https://doi.org/10.1002/ejic.202200679 Part of the Institute Feature highlighting the "Dalign University of Tech-

Part of the Institute Feature highlighting the "Dalian University of Technology". MOF-801 membrane with higher missing-linker number, which was beneficial for increasing water flux with little compromise in dye rejection rate. The MOF-801 membrane prepared in this work exhibited excellent dye rejection performance (CR rejection rate of 99.50% and water flux of $31.69 \, Lm^{-2} h^{-1} bar^{-1}$) as well as excellent long-term stability.

In recent decades, defect engineering has shown great promise in tailoring the functionality and utility of diverse MOF materials.^[26-30] For instance, relevant studies indicated that surface areas, aperture size, and pore volume of UiO-66 could be manipulated by varving missing-linker numbers.^[31-32] Ravichandar. et al. found that formic acid, which served as monodentate ligands, would compete with bidentate benzenedicarboxylic acid ligands upon coordinating with Zr₆(OH)₆O₆ clusters, resulting the generation of missing-linker in the framework, whose number was found to be positively associated with the hydrophilicity.[33] Farha. et al. found that with increasing modulator amount, the missing-ligand number would increase, resulting in larger cavity in the framework.[34] Winston Ho. et al. confirmed that defect engineering of UiO-66 membranes enabled optimization of both the pore aperture and hydrophilicity so that water flux during desalination was significantly improved.[35]

MOF-801, with the formula of $Zr_6O_4(OH)_4(O_2C-(CH)_2-CO_2)_{6r}$ represents a typical zirconium-based MOF featuring high chemical stability and hydrophilicity (Figure S1);^[36-39] moreover, the fumaric acid ligand, a natural biomass, is cheap, environmentally friendly, and easily available. Behrens. et al. pioneered the preparation of MOF-801 powders by adding formic acid, which was crucial for enhancing their crystallinity, as modulator.^[40] Relevant Monte Carlo and First Principle DFT simulations revealed that high defect density in the framework was responsible for their ultra-high water vapor adsorption capacity.^[41] Soldatov. et al. found that the grain size, crystallinity, and surface areas of MOF-801 powders increased with the addition of modulator (i.e., formic acid).^[42] Inspired by these achievements, in this study, we fabricated well-intergrown MOF-801 membranes showing excellent dye rejection performance by epitaxial growth (Figure 1 and Figure S2); of particular note, their structural deficiencies were found to exert significant influence on the separation performance.

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Figure 1. Schematic illustration of the preparation of MOF-801 membranes by epitaxial growth.

Results and Discussion

Initially, MOF-801 seeds were synthesized following a previous procedure.^[40] Our results showed that temperature, reaction time and formic acid concentration exerted significant influence on their morphology. MOF-801 seeds were prepared at reaction temperature in the range of 100–200 °C. Our results indicated that the minimum temperature required to synthesize highly crystalline MOF-801 powders was 120 °C, while with the increase of formic acid dosages, the crystallinity of MOF-801 powder gradually increased (Figure S3), and the size increased to a certain extent (Figure S4). As shown in Figure 2b, prepared MOF-801 seeds with the pore size of 0.48 nm exhibited octahedron-like appearance with an average size of 350 nm. By



Fuyuan Yan currently is pursuing her master's degree in Prof. Yi Liu's group at Dalian University of Technology. She received her bachelor's degree in 2020 from the School of Chemical Technology at Dalian University of Technology. Her research interests focus on the research of new MOFs membranes, especially MOF-801 membranes for application in water treatment.

Jiahui Yan obtained his bachelor's degree in



chemical engineering and technology from Nanjing Tech University in 2019. Then he joined the "Advanced Molecular Sieve Membrane Research Group" at Dalian University of Technology and started his PhD in chemical engineering from 2021. His research interests mainly deal with the environmentally friendly synthesis and design of defect-engineered zirconium-based MOF membranes with potential applications in gas separation.



Dr. Yanwei Sun currently worked as a postdoctoral fellow at Dalian University of Technology. She studied chemical technology at Dalian University of Technology under the supervision of Prof. Yi Liu and received her PhD in 2021. Her research interest mainly focuses on the rational design and microstructure optimization of metal-organic framework (MOF) membranes/films, especially crystallographic oriented and ultrathin Ti/Zr-MOF based membranes for energy-efficient CO₂ capture, H₂ purification, and olefin/paraffin separation.



Taotao Ji obtained his bachelor's degree in chemical engineering and technology from Central South University in 2017. Then he joined the "Advanced Molecular Sieve Membrane Research Group" at Dalian University of Technology and started his PhD in chemical engineering from 2020. His research interests mainly deal with the environmentally friendly synthesis and design of pressure-resistant porous molecular sieve membrane with potential applications in gas separation.



Yongfu He received his bachelor's degree in 2020 from the School of Chemical Technology at Dalian University of Technology. He is currently working on his master's degree in Prof. Yi Liu's group. His research focuses on the synthesis of one-dimensional molecular sieving membranes for efficient nanofiltration.



Xinwen Guo is a Professor of Chemical Engineering at Dalian University of Technology. He received his Ph.D. degree in Industrial Catalysis from Dalian University of Technology (DUT), in 1994. Currently, he is the Head of School of Chemical Engineering at DUT. His research interests are mainly focused on the catalytic conversion of carbon dioxide and molecular sieve catalysis. He has won second prize for the National Science and Technology Progress Award in 2003. He is an Editorial Board Member of Chinese Journal of Catalysis, Acta Petrolei Sinica (Petroleum Processing Section), and Chemical Engineering and Technology.



Yi Liu received PhD from Dalian Institute of Chemical Physics, Chinese Academy of Sciences in 2012. During 2012 and 2015 he worked as an Alexander von Humboldt Research Fellow at Leibniz Universität Hannover, Germany. During 2015 and 2016 he worked as a Postdoctoral Fellow at Kyoto University. Yi Liu joined Dalian University of Technology as a Professor on October 2016. His research interests include multi-scale optimization of zeolite, MOF, and low-dimensional membranes for potential use in gas separation, ion sieving, and water treatment.



Figure 2. SEM images of MOF-801 seeds obtained with (a) 0 equiv. and (b) 30 equiv. formic acid; (c) XRD patterns, (d) TGA curves under air conditions, (e) N_2 adsorption isotherms, and (f) pore size distributions of MOF-801 (0 eq) and MOF-801 (30 eq). Scale bar: 1 μ m. MOF-801(0 eq) represents MOF-801 seeds synthesized in the absence of formic acid, and MOF-801(30 eq) represents MOF-801 seeds prepared in the presence of 30 equiv. formic acid.

comparing Figure 2a–b, there was no doubt that the addition of formic acid was crucial for improving the crystallinity.

Considering the potential impact of structural deficiencies on the dye rejection performance, XRD and TG analyses were further conducted to quantify linker vacancies of the obtained MOF-801 powders (Figure 2c-d).^[29] Relevant calculation results demonstrated that missing-linker numbers per $Zr_6O_4(OH)_4$ node in the framework of MOF-801 (0 eq) and MOF-801 (30 eq) reached 0.79 and 1.83, respectively, implying that the missinglinker number increased with increasing formic acid concentration, which coincided well with previous reports.^[28] The positive relationship between missing-linker number and formic acid concentration could be attributed to competition between formic acid and fumaric acid ligands for coordinating with open metal sites in Zr-oxo clusters (Table S1).

To further explore the relationship between linker vacancies and textural properties, N₂ adsorption isotherms of MOF-801 (0 eq) and MOF-801 (30 eq) were further measured at 77 K (Figure 2e). Our results showed that both BET surface areas (from 638.6 m²g⁻¹ to 740.8 m²g⁻¹) and pore volumes (from 0.33 m³g⁻¹ and 0.46 m³g⁻¹) of MOF-801 seeds were positively correlated to the missing-linker number (from 0.79 to 1.83)

(Figure S5). Another outcome of increased missing-linker number might be enlarged pore aperture,^[34] which altogether was quite advantageous for enhancing water permeation through the membrane (Figure 2f).

Subsequently, dip-coating was conducted to deposit MOF-801 (30 eq) on porous α -Al₂O₃ tubes. Relevant SEM and XRD results manifested that the prepared 1.1 µm-thick MOF-801 seed layer was uniform and closely packed with random orientation. In addition, SEM images of the MOF-801 seed layer prepared by spin-coating were shown in Figure S6.

In the next step, epitaxial growth was conducted at reaction temperatures in the range of 100-200 °C (Figure S7-S8). Our results indicated that 120 °C was the threshold temperature capable of eliminating intergranular gaps in the seed layer. As shown in Figure 3a–f, a well-intergrown 1.3 µm-thick membrane could be obtained under optimized synthetic conditions (*i.e.*, at 120 °C for 24 h). The XRD pattern further confirmed that the prepared membrane belonged to pure MOF-801 phase with no preferred orientation (Figure 4). As expected, further elevating the reaction time or prolonging the reaction duration resulted in increased membrane thickness.

Simultaneously, the influence of modular concentration on the membrane morphology was investigated. As shown in Figure 3, under identical synthetic conditions, both MOF-801-m (0 eq) and MOF-801-m (30 eq) exhibited similar surface morphology.

Considering the potential impact of textural properties on the separation performance of MOF-801 membranes, MOF-801 powders sedimented at the bottom of the vessel after epitaxial growth were collected and subjected to characterization. Since modulator concentration was found to exert negligible influence on the morphology of MOF-801 membranes, their discrepancy in dye rejection performances could be largely attributed to different missing-linker numbers. Our results





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Figure 4. XRD patterns of (a) MOF-801 (30 eq) seed, (b) MOF-801(30 eq) seed layer, and (c) MOF-801-m (0 eq).

indicated that being similar to MOF-801 seeds, missing-linker numbers in the framework of MOF-801-m (0 eq) and MOF-801m (30 eq) reached 0.95 and 2.43, respectively. We also measured the adsorption/desorption curve, specific surface area, pore size distribution and other data of MOF-801 powder of the bottom product using N₂ physical adsorption method. The BET surface area and micropore volume were calculated as 866.4 $m^2 g^{-1}$ and 0.37 $m^3 g^{-1}$ for MOF-801 (0 eq), and 952.1 $m^2 g^{-1}$ and 0.49 $m^3 g^{-1}$ for MOF-801 (30 eq), respectively. Simultaneously, the pore size distribution calculated by Horvath Kawazoe method showed that the median pore sizes of MOF-801 (0 eq) and MOF-801 (30 eq) were 0.52 nm and 0.60 nm, respectively, indicating that both their BET surface areas and pore volume were positively correlated to the missing-linker number. We therefore concluded that the addition of formic acid led to higher missing-linker number, which in turn caused increased surface areas and enlarged pore aperture (Figure S9).

We finally measured dye rejection performances of Conge Red (CR), Calcein (CA), and Methylene Blue (MB) on the obtained MOF-801 membranes. Our results (Figure S10-S13) indicated that MOF-801-m (0 eq) maintained excellent rejection rates towards CR (99.73%), CA (99.41%), and MB (99.16%). The discrepancy in separation efficiency among three dyes was dominated by size-exclusion effect since their rejection rates were in good agreement with molecular sizes: CR (25 Å) > CA (15 Å) > MB (12 Å) (Table S2); in addition, we found that water fluxes of three dyes were strongly dependent on their 2potential (-33.2 mV for CA, -0.55 mV for CR, 2.14 mV for MB) in aqueous solutions, while the ζ -potential of MOF-801 seed suspension was 20 mV. So we believed that the charge might not be the key factor affecting the water fluxes of different dye molecules, but the size screening was. Because the molecular size of the MB dye was the smallest, it was easy to embed into the channels of the MOF-801 membrane, causing the blocking of the screening channels and therefore, reduced water flux.^[16] Comparation of the separation performance of the MOF-801 membrane with the literature was shown in Figure S14 and Table S3.

We further investigated dye rejection performance of the MOF-801 membrane in a cross-flow interception mode. Our results implied that its CR rejection rate and water flux achieved 99.50% and $31.69 \text{ L} \cdot \text{m}^{-2} \text{h}^{-1} \text{ bar}^{-1}$, respectively, which was superior to most pure MOF membranes reported so far (Figure 5); moreover, the influence of operation pressure on the dye rejection performance was studied. It was observed that the rejection rate decreased slightly (from 99.8% to 95.0%) with increasing pressure, while the water flux remained stable at higher pressure (~31 L $\cdot \text{m}^{-2}\text{h}^{-1}\text{ bar}^{-1}$, Figure 6a). The results from long-term stability test revealed that there was no obvious change in both CR rejection rate and water flux within 40 h, thus confirming long-term operation stability of the obtained MOF membrane (Figure 6b).

To elucidate the impact of missing-linker number on dye rejection performance, besides MOF-801-m (0 eq), MOF-801-m



Figure 5. CR dye rejection performance of MOF-801-m (0 eq) and MOF-801-m (30 eq) supported on porous α -Al₂O₃ tubes. Dye concentration: 100 mg/L, room temperature, pressure: 1 bar.



Figure 6. (a) Effect of operating pressure on CR rejection performance on porous α -Al₂O₃ tube of MOF-801-m (0 eq). (b) Long-term stability on CR rejection performance on porous α -Al₂O₃ tube of MOF-801-m (0 eq). (c) Effect of operating pressure on CR rejection performance on porous α -Al₂O₃ tube of MOF-801-m (30 eq). (d) Long-term stability on CR rejection performance on porous α -Al₂O₃ tube of MOF-801-m (30 eq). (d) Long-term stability on CR rejection performance on porou α -Al₂O₃ tube of MOF-801-m (30 eq).

(30 eq) was further subjected to CR rejection tests (Figure 6c-d). Our results indicated that the MOF-801-m (30 eq) exhibited higher flux at the expense of lower CR rejection. This was understandable, since the introduction of formic acid caused higher missing-linker number, which, in turn, led to enlarged pore aperture and pore volume (i.e., lower rejection rate). To verify the correlation between the missing-linker number and water flux, we further explored the influence of formic acid concentration on the water contact angle of the prepared membrane. As shown in Figure 7, compared with MOF-801-m (0 eg) (~46°), the water contact angle of the MOF-801-m (30 eg) was smaller (~20°), thus confirming that the MOF-801 (30 eq) membrane was more hydrophilic (i.e., higher water flux). In effect, the synergistic relationship between formic acid concentration and membrane hydrophilicity (i.e., water flux) was confirmed by previous reports either.[33,35,41]

Conclusion

To summarize, in this study, we prepared defect-engineered polycrystalline MOF-801 membrane by epitaxial growth. It was found that not only the crystallinity but also the missing-linker number could be facilely tuned through varving the concentration of formic acid. The obtained membrane manifested superior dye rejection performances (rejection rate >99.50% and water flux > 31.69 L \cdot m⁻² h⁻¹ bar⁻¹). Of particular note, we found that the missing-linker number was positively associated with the water flux with little compromise in dye rejection rate.

Experimental Section

Materials: Zirconium chloride (ZrCl₄, 98%, Maclin), fumaric acid (C₄H₄O₄, 99.5%, Maclin), formic acid (HCOOH, 98%, Maclin), N,Ndimethylformamide (DMF, 99.8%, Tianjin Kemiou), methanol (CH₄O, 99.5%, Macklin), ethanol (C₂H₆O, 99.7%, Tianjin Kemiou), Congo red (CR, Biological dye, Maclin), Calcein (CA, Biological dye, Maclin), and Methylene blue (MB, Biological dye, Maclin) were used as received without further purification. Both porous α -Al₂O₃ disks and tubes were acquired from Fraunhofer IKTS, Germany.

Synthesis of MOF-801 seeds: MOF-801 seeds were synthesized as reported in the literature with slight modification. Initially, 0.120 g

Figure 7. Contact angles of (a) MOF-801-m (0 eq)-ST (~46 °) and (b) MOF-

801-m (30 eq)-ST (\sim 20 °). ST denotes the starting time for the contact of the liquid droplet and membrane face.

 $ZrCl_4$ and 0.180 g $C_4H_4O_4$ were dissolved in 20 ml DMF. Subsequently, 0.714 g HCOOH was added in the above solution, followed by vigorous stirring for 30 min. In the next step, the above solution was placed in an oven at 120 °C for 24 h to form white precipitates. Finally, the precipitates were separated by high-speed centrifugation (8000 rpm, 5 min), washed with DMF and anhydrous ethanol for 3 times, and dried overnight for further use.

Preparation of MOF-801 seed layer: The MOF-801 seed layer was obtained via dip-coating. Initially, 0.5 g MOF-801 seeds were added in 50 mL ethanol. Subsequently, the above suspension was dispersed by sonication and stirred at room temperature for at least 3 days before use. In the next step, a porous α -Al₂O₃ tube with length of 5 cm was sealed with Teflon tape on both sides after HCI treatment. The whole tube was then immersed in the above suspension for 20 s and manually pulled up at a speed of 0.125 cm/ s. Finally, the MOF-801 seed layer was dried overnight at room temperature.

Epitaxial growth of the MOF-801 seed layer: Initially, 0.180 g ZrCl₄ and 0.270 g $C_4H_4O_4$ were dissolved in 30 ml DMF. After blocking both ends with PTFE supports, the porous α -Al₂O₃ tube was vertically placed in the precursor solution. Epitaxial growth was conducted at 120°C for 24 h in an oven. Finally, the obtained membrane was washed with anhydrous methanol and dried overnight before further use.

Dye rejection tests: All dye rejection data were obtained from membrane modules in cross-flow mode. Schematic illustration of the dye rejection test was shown in Figure S2. The MOF-801 membrane with an effective area of 18.84 cm² was used to evaluate the separation performance. The concentration of dye-containing solution was maintained at 0.1 g/L (Table S1). Each membrane was tested under 1 bar transmembrane pressure (TMP). The temperature of the feed side was maintained at 25 ± 1 °C. To ensure the accuracy of experimental results, each membrane was tested at least three times under identical operation conditions. In addition, long-term stability test was conducted at 1 bar. Water flux (J), rejection rate (R) and water flux (A) were calculated based on the following equation:

$$J = \frac{\Delta V \text{feed}}{Am \cdot \Delta t} \tag{1}$$

where ΔV feed (L) represents the volume of the permeate solution, Δt (h) represents the operation time interval, and Am (m²) is the effective membrane area.

$$R = \frac{C_f - C_p}{C_f} \cdot 100\%$$
⁽²⁾

$$A = \frac{J}{\Delta p}$$
(3)

Characterization: The morphology of MOF-801 seeds, seed layers and membranes were characterized by SEM (U1000, Hitachi Co.). The phase purity was determined by XRD (Rigaku Smart Lab diffractometer) using Cu-K_a radiation (λ =0.15418 nm) with the 1°/ min scan rate and 5-50° scan angle. Physical adsorption analysis was conducted on Mike ASAP 2020 Plus. TGA results were conducted on NETZSCH (TG 209) thermal analyzer under air or N₂ atmosphere. UV-vis spectra were obtained from Jasco V-570 with the scanning range of 200-800 nm.





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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: Dye rejection · Membrane · Metal-organic framework · MOF-801 · Structural deficiency

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RESEARCH ARTICLE

Well-intergrown MOF-801 membranes were presented with different defects, which showed excellent dye rejection performance by epitaxial growth. The control of the structure and function of MOF-801 membranes by formic was presented so that their separation performances could be deliberately tailored. This strategy would promote the further development of defect engineering to improve the performance of MOF membrane.



F. Yan, J. Yan, Dr. Y. Sun, T. Ji, Y. He, Prof. X. Guo*, Prof. Y. Liu*

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Fabrication of Defect-Engineered MOF-801 Membrane for Efficient Dye Rejection