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**Self-modified fabrication of inner skin ZIF-8 tubular
membranes by counter diffusion assisted secondary growth
method**

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To RSC Advances

Abstract:

The ability to fabricate high-quality MOF-based membranes is critical and highly desired due to their outstanding performance in molecule separations and sensors. In this work, water stable MOF, ZIF-8 is chosen as the typical example to validate a new self-modified counter diffusion assisted secondary growth method for the fabrication of inner skin tubular MOF membranes. The preparation route involves two main steps: the counter diffusion for modifying the rough surface of industry ceramic substrate (plugging pores in the ceramic tube) with homogenous ZIF-8 nanocrystals, and the secondary solvothermal growth for fabricating continuous ZIF-8 membranes on the inner surface of the tube substrate. The ZIF-8 membranes prepared by this method are characterized in detail. The pre-modified process and the use of a low-reactivity growth solution containing zinc acetate favor the growth of dense ZIF-8 membrane in the solvothermal process.

Keywords: counter diffusion, secondary growth, self-modified, ZIF-8 membrane

Introduction

The potential of metal-organic frameworks (MOFs) as membrane materials has already been recognized both experimentally and computationally.¹ The development of MOF membranes for their potential applications as separators, reactors, and sensors has attracted tremendous attention in recent years.^{2,3} However, the controlled deposition of homogeneous MOF membranes that are free of defects and stable under harsh operation conditions on different substrates is a challenge in each particular case.

There are numerous methods for preparing MOF-based membranes including the direct growth method without^{4,5} or with substrate modification,^{6,7} step-by-step method,⁸⁻¹⁰ the secondary growth method with various strategies for seeding layer,¹¹⁻²⁴ and the counter diffusion method,²⁵⁻²⁹ along with other techniques.^{30,31} The MOF membranes prepared by the secondary growth method often have a good quality, and the counter diffusion method can lead to the formation of precise molecular-sieve membranes on porous supports.

Although achieving an enormous progress in making MOF membranes, on the other hand, most of them have been prepared on the flat discs of limited size, which limit their large scale applications. Some efforts have also been made for the tubular MOF membranes,^{11,15,22,23,32} but the usually used α -Al₂O₃ tubes need a buffer layer of 100-200 nm pore size, as well as the surface active modification, which complicate the fabrication processes. Simultaneously, the reproducibility and scalability of the resulting membranes still remain a difficult challenge so far. The development of new methods for fabricating MOF membranes is thus crucial in this research topic.

In this work, we developed a counter diffusion assisted secondary growth method to fabricate tubular MOF membranes on the inner surface of α -Al₂O₃ ceramic tubes. Here the water stable ZIF-8 MOF membrane, as a typical example, was successfully fabricated by this new method. The industry α -Al₂O₃ ceramic tube supports, without any fine treatment such as adding buffer layers or polishing surface were used in this

work. The preparation route involved two main steps: an efficient counter diffusion approach for self-modifying the ceramic substrate (plugging pores in the ceramic tube) with homogenous ZIF-8 nanocrystals, and secondary solvothermal growth for fabricating continuous ZIF-8 thin films on the inner surface of the ceramic tube. Herein, we report this new method for the successful fabrication of ZIF-8 membranes, acting as an experimental proof-of-concept.

Experimental section

Chemicals

The chemicals and reagents used for the membrane preparation include zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98.0%), zinc acetate dehydrate ($\text{Zn}(\text{OAc})_2$, $\geq 98.0\%$), sodium formate dehydrate (HCOONa , $\geq 99.5\%$), cetyltrimethylammonium bromide (CTAB, 99.0%) and ethanol anhydrous, methanol anhydrous ($\geq 99.5\%$) for the growth of the ZIF-8 membrane. Except for 2-methylimidazole (Hmim, 99.0%) purchased from Sigma-Aldrich Chemical. Co. Ltd., the rest of the chemicals were all supplied by Sinopharm Chemical Reagent Co. Ltd. All chemicals were used without further purifications. Porous ceramic tubes were purchased from Jiexi Lishun limited company, which were cut into 100 mm lengths and washed repeatedly with distilled water to remove dirt and impurities before drying in an oven at $100\text{ }^\circ\text{C}$ for 5 h, for the membrane fabrication.

Self-modification of ceramic tubes

Typically, a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.297 g) in 10 mL of methanol was rapidly poured into a mixture solution of Hmim (0.598 g) and CTAB (0.018 g) in 10 mL of methanol under stirring. The molar ratio of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$:Hmim:CTAB is 1:7.3:0.05. The operation was performed at room temperature. A clear solution can be obtained, and subsequently was poured into the ceramic tube sealed with rubber plug immediately. Then, the tubular ceramic substrate was placed horizontally in an airtight container and stayed at $55\text{ }^\circ\text{C}$ for 4 h, followed by drying at $55\text{ }^\circ\text{C}$ for 1 h. The

ceramic tube was then rinsed with methanol and dried at 25 °C for 12 h.

Preparation of continuous ZIF-8 membranes

The typical solvothermal growth solution was prepared by dissolving in sequence 1.578 g of Zn(OAc)₂, 5.860 g of Hmim, and 0.600 g of HCOONa in 100 mL of methanol under stirring for 20 min at room temperature. The self-modified ceramic tube was then immersed in the growth solution in Teflon autoclave and heated in a convection oven at 110 °C for 24 h. The autoclave was then removed from the oven and allowed to cool naturally to room temperature. After that, the ceramic tube was washed with methanol and dried in ambient conditions for 1 day.

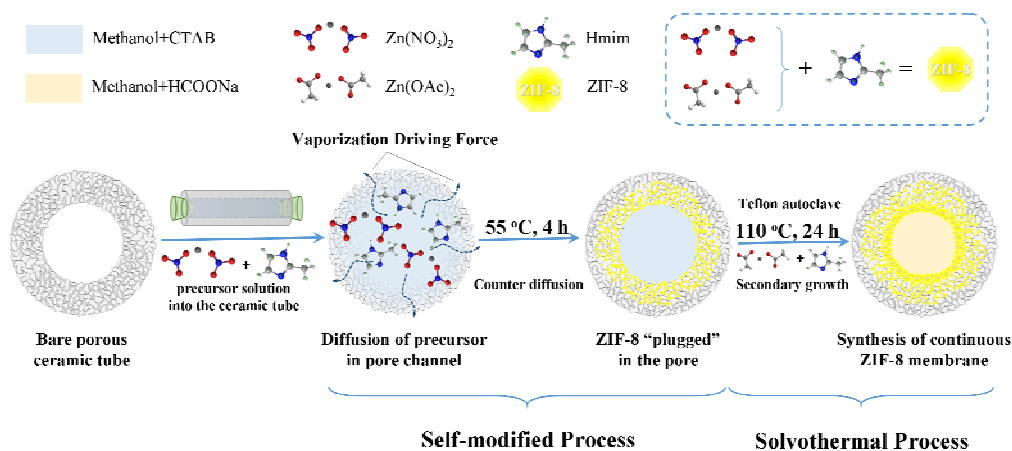
Characterization

Powder X-ray diffraction (PXRD) patterns were collected with a Bruker D8 powder X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Diffraction data were collected at room temperature in the range of $2\theta = 5^\circ\sim 40^\circ$ with 0.02° steps. The morphology of growth solutions was determined on a Hitachi Model H-800 instrument. Fourier-transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Fourier transform infrared spectrometer, by using attenuated total reflectance technique for the films and KBr technique for the Hmim powder. Scanning electron microscopy (SEM) and element mapping images were collected using a FEI Nova Nano 230 instrument with the acceleration voltage of 3 kV.

Results and discussion

In the present method, the precursor solution in the self-modification process is composed of zinc nitrate, excess amount of Hmim molecule, small amount of CTAB, and methanol is used as solvent with high vapor pressure. When the precursor solution was put into the inner side of the tubular ceramic substrate, the ZIF-8 nanocrystals formed and gathered into the pore induced by the driving force from the evaporation of methanol, as illustrated in Scheme 1. Thus the reaction continues within the porous ceramic tube until the pores are fully plugged by the generated

ZIF-8 nanocrystals.



Scheme 1 Preparation scheme of the counter diffusion method for plugging pore and secondary growth method for ZIF-8 membrane on the inner surface of a ceramic tube.

It should be pointed out that CTAB in the precursor solution has played an important role in the self-modification process. On the one hand, CTAB with $-NH_2$ groups could control the growth of ZIF-8 crystals to obtain small particles. On the other hand, CTAB could reduce the surface tension of the precursor solution, leading to a good microscopic permeability, and meanwhile effectively avoid the occurrence of leakage of solution from the porous ceramic substrate.

In the secondary growth solution, $Zn(OAc)_2$ is chosen as zinc source instead of $Zn(NO_3)_2$, and $HCOONa$ is used as inducing agent for the formation of ZIF-8 phase. As we known, the acetic acid anion (OAc^-) and the Zn^{2+} ion can form a chelate structure in the methanol solution, so that $Zn(OAc)_2$ can be considered to be a pre-organized zinc source. This pre-organization may inhibit the ligand exchange, thus decreasing the formation rate of the ZIF-8 phase.³³ Therefore, $Zn(OAc)_2$ could allow for enough zinc ions and Hmim ligands reacting on the surface of plugged ceramic tube during the secondary growth, which is also an essential factor for preparing intense ZIF-8 membranes in this work.

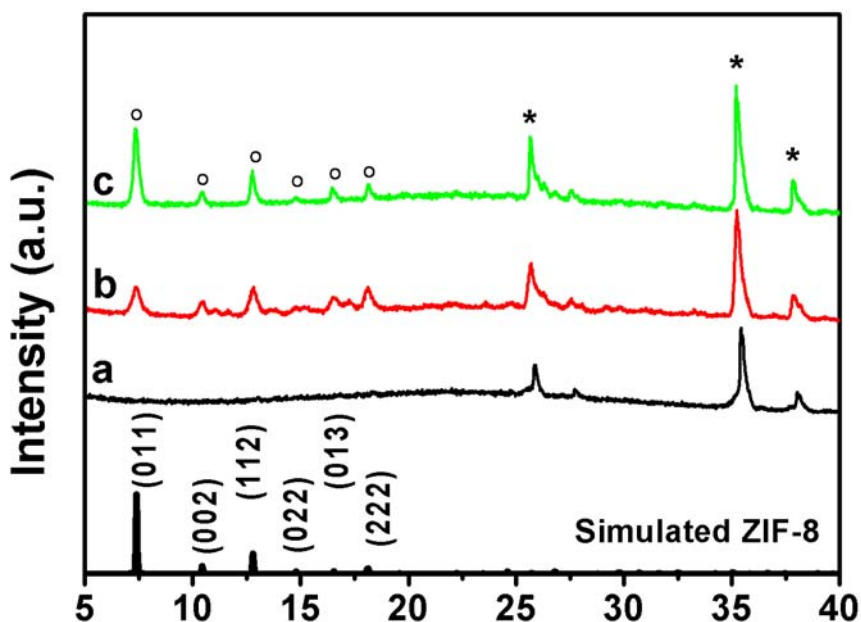


Fig. 1 PXRD patterns of the (a) bare α - Al_2O_3 substrate, (b) α - Al_2O_3 substrate after self-modified process, (c) ZIF-8 membrane formed after secondary growth, and the simulated one from ZIF-8 crystal structure data excluding guest species. Peaks marked with circles and asterisks represent diffraction peaks from ZIF-8 membrane and ceramic substrate, respectively.

Fig. 1 shows the PXRD patterns of the bare α - Al_2O_3 substrate, α - Al_2O_3 substrate after the self-modified process and the finally fabricated ZIF-8 membrane after secondary growth treatment. It shows that diffraction peaks of secondary growth sample match well with the pattern simulated from the published ZIF-8 crystal structure data,³⁴ so that the formed layer together with the one after solvothermal treatment indeed belong to the ZIF-8 phase. Moreover, the membranes display a strong intensity in the (011) reflection related to other reflections, indicating a preferred crystal orientation of the (011) planes parallel to the ceramic support. The PXRD pattern of the α - Al_2O_3 substrate sample after the self-modification process is similar to the one after the secondary growth in the diffraction peak positions, but the peak intensity increases obviously after the solvothermal treatment, indicating the following solvothermal secondary growth is beneficial for growing ZIF-8 membrane on the inner surface of ceramic tube, and improving crystallinity of the ZIF-8 membrane.

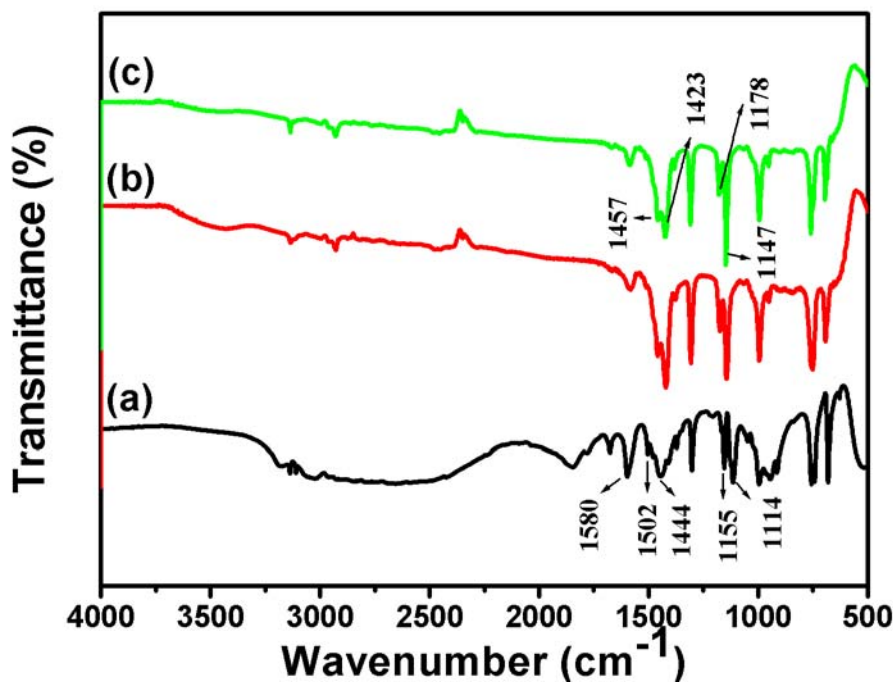


Fig. 2 FTIR spectra of (a) pure Hmim, (b) self-modified sample, and (c) ZIF-8 membrane after secondary growth.

FTIR spectra of pure Hmim, self-modified substrate sample, and the ZIF-8 membrane after secondary growth treatment are shown in Fig. 2. The peak at about 1580 cm^{-1} in pure Hmim (Fig. 2a) could be assigned as the C=N stretching vibration. The intense and convoluted bands at about 1444 and 1502 cm^{-1} are associated with the entire ring stretching of Hmim. In the samples of ceramic substrate after self-modification (Fig. 2b) and secondary solvothermal treatment (Fig. 2c), the two bands shift towards lower frequency to 1423 and 1457 cm^{-1} , respectively. The other two bands at 1114 and 1155 cm^{-1} belonging to the in-plane bending of the Hmim ring, undergone blue shifts to 1147 and 1178 cm^{-1} , respectively. While those below 800 cm^{-1} can be assigned as out-of-plane bending of Hmim ring. The shifts in absorption bands indicate that Zn ions strongly interact with the Hmim ligands. The FTIR spectrum of plugging sample is thus in good agreement with the ZIF-8 membrane treated with solvothermal process and also with pure ZIF-8 prepared according to the literature.^{27,35,36}

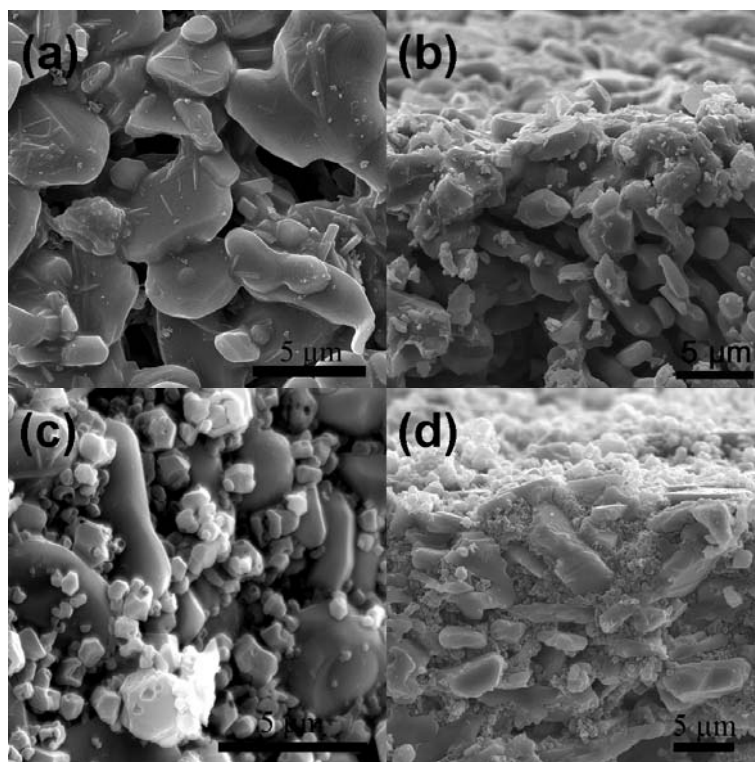


Fig. 3 SEM images of (a) the surface and (b) the cross section view of the bare α -Al₂O₃ substrate, (c) the surface and (d) the cross section view of α -Al₂O₃ substrate after the self-modification.

Asymmetric porous α -Al₂O₃ tubes (diameter 13 mm, thickness 2 mm and length 100 mm) without α -Al₂O₃ buffer layers and surface active modification are used as supports. Fig. 3a and 3b show the SEM images of the bare α -Al₂O₃ support. It is clear that the inner surface of the tube is consisted of coarse α -Al₂O₃ particles with irregular size and shape, and with pore diameters between 1 and 3 μ m. The pores of the ceramic tube are plugged by ZIF-8 nanoparticles after the self-modification treatment, and the coarse α -Al₂O₃ particles are still observed (see Fig. 3c). This counter diffusion process of plugging holes is the first step and also crucial for the growth of the ZIF-8 membranes. With the evaporation of methanol solvent, ZIF-8 nanoparticles gathered and deposited in the pores, finally fully plugged the channel holes as shown in Fig. 3d.

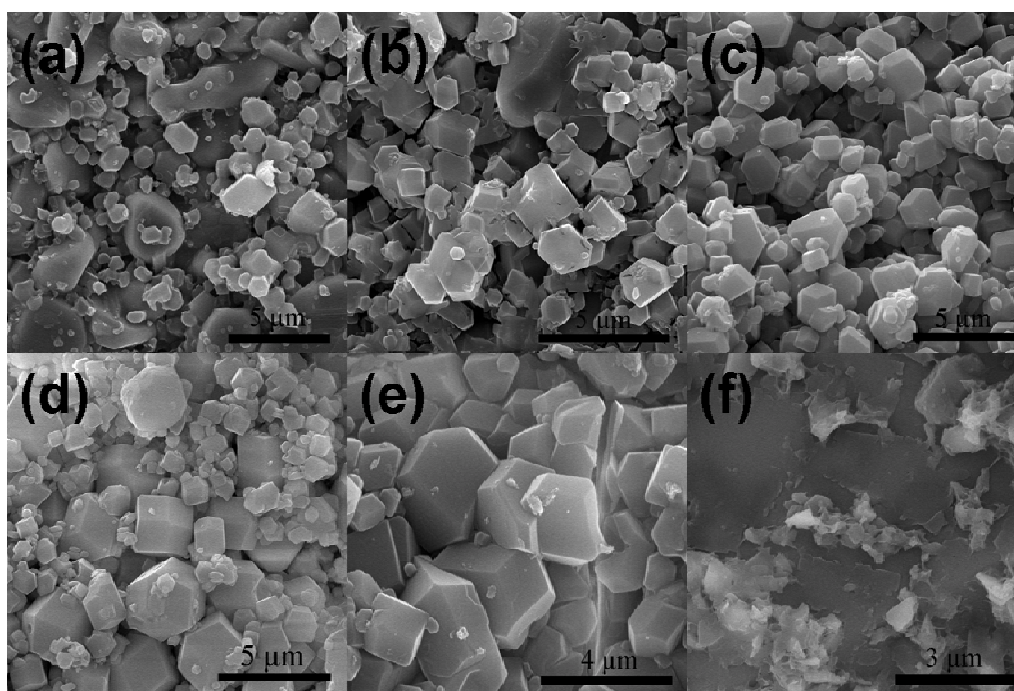


Fig. 4 The SEM top view of the prepared ZIF-8 membrane after solvothermal treatment at 110 °C for different times (a) 2 h, (b) 4 h, (c) 6 h, (d) 12 h, (e) 24 h, and (f) at 120 °C for 24 h.

In the meantime, the rest of unreacted Hmim molecules in precursor solution might adsorb and adhere to the surface of α -Al₂O₃ substrate to create active sites for the nucleation of ZIF-8 via a van der Waals attraction,⁷ which could realize the self-modification for the inner surface of ceramic tube, and contribute to the formation of continuous ZIF-8 membrane in the following solvothermal process. Our results verified that the ZIF-8 nanoparticles gradually deposited on bare α -Al₂O₃ support and grew obviously in the following secondary growth process with the increase of solvothermal reaction time at 110 °C (see Fig. 4a-e), and finally continuous ZIF-8 membranes formed. A more compact ZIF-8 deposition and growth on the self-modified ceramic supports can be clearly seen in Fig. 4f, taken from the top-view of membrane, after the solvothermal treatment at 120 °C for 24 h.

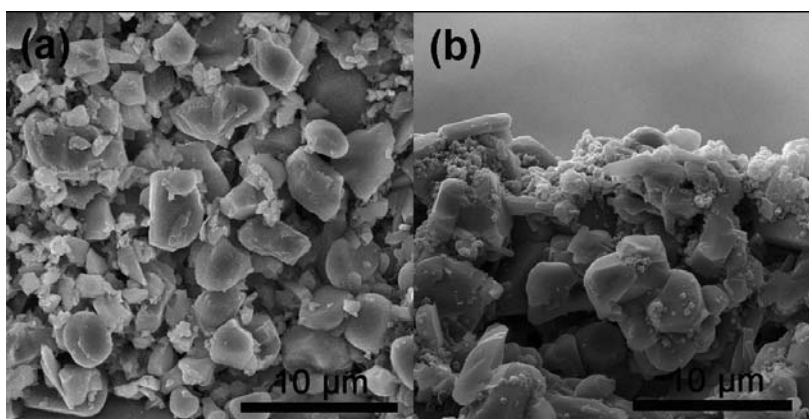


Fig. 5 SEM images of (a) surface and (b) cross section view of α -Al₂O₃ support directly through solvothermal treatment without self-modified process (scale bar = 10 μ m).

For comparison, we also tried to directly grow a continuous ZIF-8 layer on the porous α -Al₂O₃ tube without self-modification process, but failed in our several attempts. The SEM images (see Fig. 5a and b) show that ZIF-8 crystals are not packed well in the pore channels, and are discontinuous on the inner surface of α -Al₂O₃ tube. It is clear, the ZIF-8 crystals are easier to grow in the solvothermal solution than on the α -Al₂O₃ support, which demonstrates that the self-modified process with ZIF-8 nanoparticles is very important in the formation of a defect-free ZIF-8 membrane on the inner surface of the α -Al₂O₃ tube.

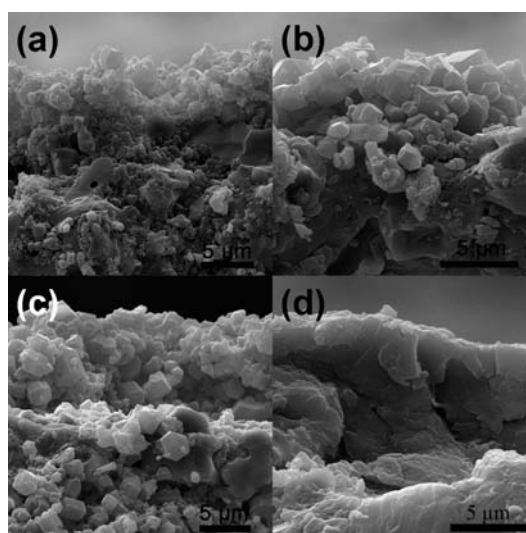


Fig. 6 The cross section view of ZIF-8 membranes on the α -Al₂O₃ support at different solvothermal temperatures (a) 90 °C, (b) 100 °C, (c) 110 °C, and (d) 120 °C (scale bar = 5 μ m).

The SEM images (Fig. 6a-d) also show that well inter-grown and compact ZIF-8 membranes are appended on the inner surface of the α -Al₂O₃ support, and the membrane thickness can be controlled by increasing the solvothermal reaction temperature. It was observed that the membrane well intergrown from the membrane surface to the self-modification support over an entire thickness of about 4 μ m after solvothermal treatment at 90 °C. The thickness of the ZIF-8 membrane increases to about 8 μ m after increasing the solvothermal temperature to 120 °C, and the sizes of crystal particles increase obviously with enhancing solvothermal temperature. This result also indicates that good reproducibility of the membranes can be obtained by following this synthesis procedure.

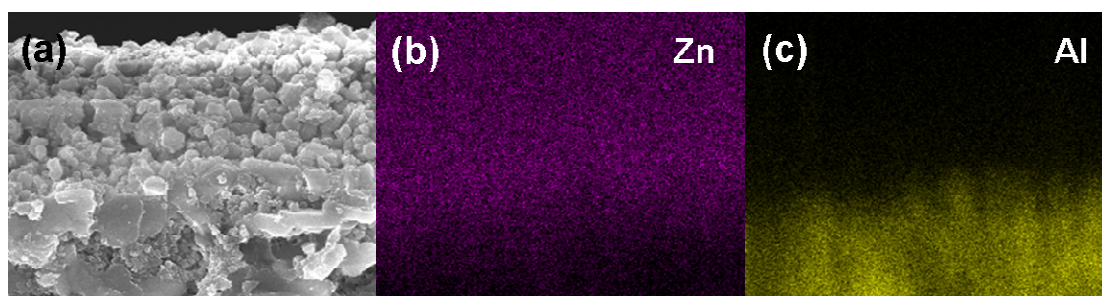


Fig. 7 SEM images of (a) the typical ZIF-8 membrane on α -Al₂O₃ support and the typical elemental mapping images of (b) zinc, and (c) aluminum.

To further realize and investigate the microstructure and elemental distribution of the ZIF-8 membrane grown on the self-modification support, scanning electron microscopic elemental mapping is explored. A SEM image and the typical corresponding elemental mapping images of zinc and aluminum are shown in Fig. 7. The uniform and continuous distribution of zinc element on ceramic support confirms the homogenous growth of the ZIF-8 layer on the inner surface, as well as the pore channels of the ceramic support. In addition, the existence of aluminum element can be assigned to the ceramic support, which is identical with the above PXRD characterization. The zinc element and aluminum element have a part cross each other, which verifies that the self-modified process indeed helps to plug the ZIF-8 into the

pore of ceramic tube.

It has been reported that pre-loaded Hmim ligand can induce the crystallization nucleation of ZIF-8 and is conducive to the growth of ZIF-8 membranes,^{7,37} which is in good agreement with our observation. However, it should be pointed out that our strategy here is different from others. Both plugging pores with ZIF-8 nanoparticles and adsorbing Hmim ligands on the surface of support occurred in the self-modification process through the counter diffusion pathway, not only realize the self-modification for inner surface of ceramic tube, but also create the homogeneous nucleation sites for the growth of continuous ZIF-8 membranes during the following solvothermal process. This counter diffusion assisted secondary growth strategy, thus, makes possible to obtain a reproducible and scalable ZIF-8 membrane on the inner surface of porous ceramic tubes without requiring fine treatment such as adding buffer layers or polishing even surface.

Conclusions

In conclusion, ZIF-8 membranes were successfully prepared on the inner surface of α -Al₂O₃ ceramic tube by a newly developed counter diffusion assisted secondary growth method. This counter diffusion approach realized both the fully plugging of pore channel of α -Al₂O₃ ceramic tube by using ZIF-8 nanoparticles under the solvent evaporation forces, and ligand modification on the inner surface of ceramic support, which favor the growth of the membrane. The use of high-reactivity colloidal solution containing zinc nitrate could lead to the self-modified process in the pore of ceramic support. While the use of low-reactivity growth solution containing zinc acetate allowed the growth of the dense ZIF-8 membrane in the solvothermal process. Compared with other methods, the present method is simple and has a good reproducibility. We believe that this new method could also extend to the fabrication of other inner skin tubular MOF membranes. Furthermore, the permeation behaviors of these ZIF-8 membranes for single small gas molecules and binary gas mixtures are testing in our lab and results would be reported in due course.

Acknowledgments

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