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A ZIF-71 Hollow Fiber Membrane Fabricated by Contra-Diffusion

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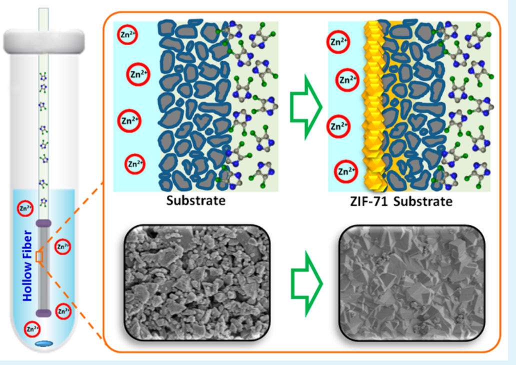
Supporting Information

ABSTRACT: As a subclass of metal−organic framework materials, zeolitic imidazolate frameworks (ZIFs) have exhibited great potential for numerous applications because of their special three-dimensional structure. Up to now, utilizing ZIF membranes for liquid separations is still limited because it is very difficult to select suitable materials and to fabricate integrated membranes. In this work, a modified contra-diffusion method was carried out to prepare ZIF-71 hollow fiber membranes. The metals Zn^{2+} and the organic links imidazole would meet and react on the interface of ceramic hollow fiber through diffusion. The as-prepared ZIF-71 membrane exhibits good performance in separation of ethanol−water mixtures.



KEYWORDS: *ZIF-71, hollow fiber, membrane, contra-diffusion, separation*

There has been extensive interest in metal−organic framework materials (MOFs) because of their versatility in tuning their structures and functionalities.[1] As a subclass of MOFs, zeolitic imidazolate frameworks (ZIFs) with extended three-dimensional structure and zeolite-like topology are formed via coordination between metal centers and organic imidazole linkers.[2] Because of permanent porosity and high thermal and chemical stability, ZIFs are attractive candidates for numerous applications, such as catalysis, adsorption, and gas separation.[3,4] Especially, ZIFs exhibit great potential as separation membranes.[5] Up to now, many inspiring studies about ZIF membranes were reported.[6−8] However, these works mainly focused on gas separations, such as CO_2 capture,[9,10] hydrogen purification,[11,12] and hydrocarbon separation.[13] Utilizing ZIF or even MOF membranes for liquid separations is limited because it is very difficult to select suitable materials and to fabricate integrated membranes. Given the rapid interesting interest in liquid separations, more studies on the ZIF or MOF membranes that are applied to organic solvent operational environments are rapidly required.[5]

Recently, hydrophobic ZIFs have been widely synthesized via designing special structures or introducing hydrophobic functional groups.[14] Their designed and tunable organic adsorption properties give us an interest to prepare hydrophobic ZIF membranes for removing organic from solvent such as ethanol−water separation.[15] First of all, choosing a suitable ZIF material is the prerequisite for fabricating an integrated and high-efficiently hydrophobic ZIF membrane. Many properties should be considered, not only including the thermal and chemical stability, but also containing the pore size, structure, and surface chemistry. Among ZIF materials, RHO-type ZIF-71 with a small window (0.48 nm) and big cages (1.68 nm) exhibits high ethanol−water selectivity.[16,17] Its intrinsic organophilic property and suitable structure make ZIF-71 a promising material for preparing hydrophobic ZIF membranes.

Dong et al. has prepared a ZIF membrane on the ZnO disk support by the reactive method and successfully used for organic solvent separation.[18] But the high resistance of the support had a great inhibition on the flux that restricted the application of ZIF membranes. Compared with ZnO disk supports, ceramic α-Al_2O_3 hollow fiber supports not only exhibit excellent chemical and thermal stabilities,[19] but also have many other advantages, such as high-packing density and cost-effective.[20] More importantly, because of its asymmetric structure (i.e., a thin separation dense layer integrated with porous layers on either side or both sides), the resistance of ceramic hollow fiber supports is rather low.[6,13,21] All these outstanding features of ceramic hollow fiber supports may drive the ZIF hollow fiber membrane to show better performance, even into commercial applications. Up to now, only a few MOF or ZIF hollow fiber composite membranes have been fabricated for gas separation.[13,22,23] In this study, we aim to prepare the ZIF-71 membrane on the ceramic hollow fiber support and to explore its separation performance of recovery of ethanol. To decrease the formation of cracks and defects during the solvent removal activation process, methanol is selected as solvent.[24]

For preparing the integrated ZIF membranes, a secondary growth method has been proven to be a feasible and effective method. Using secondary growth method, Pan et al. successfully fabricated a ZIF-8 membrane on the YSZ hollow

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fiber supports.[13] However, we found that it is very difficult to prepare ZIF-71 hollow fiber membranes by the secondary growth method, because the reaction of ZIF-71 under methanol condition is too fast and cannot be easily controlled. As shown in Figure S1 in the Supporting Information, the ZIF-71 crystals were almost formed instantly. Based on this phenomenon, the concept "contra-diffusion" could be a useful method to prepare ZIF-71/ceramic hollow fiber composite membranes. Several ZIF-8 membranes have been successfully fabricated by contra-diffusion method so far.[25,26] In addition, the fast reaction rate for the contra-diffusion method could be more benefit to make a thinner ZIF-71 layer.[27] Herein, we employed the modified contra-diffusion method to prepare the target membrane. Figure 1 shows the schematic of the preparation processes of

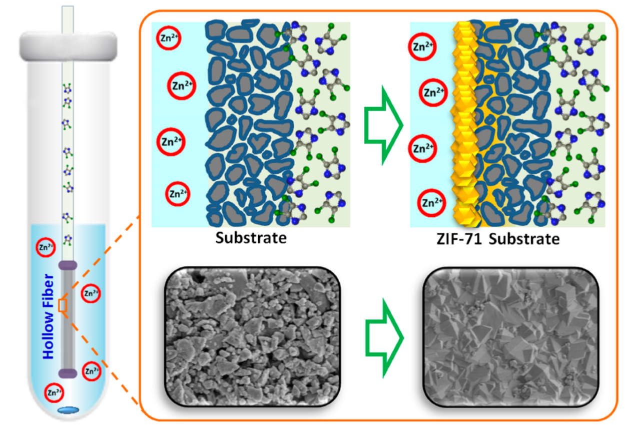

Figure 1. Schematic of preparation of ZIF-71 hollow fiber membrane by contra-diffusion.

the ZIF-71 hollow fiber membrane. A solution of the metal center and a solution of the imidazole were placed on both sides separately. Under diffusion, the metals Zn^{2+} and the organic links imidazole would meet and react on the interface of the ceramic hollow fiber support. To maintain an adequate supply of nutrients for crystal growth, an extended glass tube was vertically connected to the lumen of the ceramic hollow fiber. It is worth noting that the increased gravitational potential energy of the solution in the inner side has advantage to form defect-free membranes because more nutrients would easily pass through the defect under gravity.

The morphologies of the ZIF-71 hollow fiber membrane were surveyed using field emission scanning electron microscope (FESEM). Figure 2a shows the morphologies of the ceramic α-Al_2O_3 hollow fiber supports. The outer diameter and inner diameter of the ceramic hollow fiber were ~1.9 mm and 1.1 mm, respectively. As shown in Figure 2b, the surface of the membrane is homogeneous and free of cracks. A high degree of intergrowth within the ZIF-71 membrane could be observed. The average size of the crystals is about 2−4 μm. Figure 2c illustrates that the membrane is well boned with the ceramic hollow fiber support and the membrane thickness is about 2.5 μm. The energy-dispersive X-ray spectroscopy (EDX) of the cross-section of the membrane (Figure 2d) reveals that there is a slight penetration of ZIF-71 into the ceramic α-Al_2O_3 hollow fiber support due to the diffusion of the nutrients. This slight penetration makes the membrane intimately contact with supports. The corresponding X-ray diffraction (XRD) patterns (Figure S2 in the Supporting Information) show that the crystal structure of the membrane is consistent with the ZIF-71 pattern

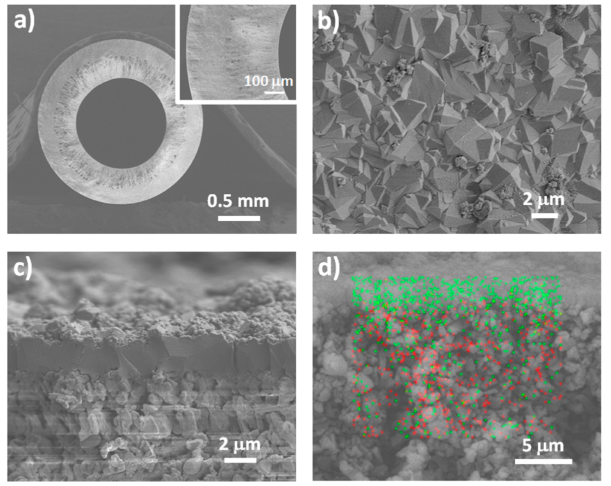

Figure 2. SEM images of (a) a ceramic hollow fiber (inset: an enlarged cross-section of the ceramic hollow fiber), (b) ZIF-71 membrane surface, and (c) ZIF-71 membrane cross-section. (d) EDX image of the cross-section of the membrane cross-section (Zn, green, Al, red).

reported in the literature.[16] To further prove that the as-prepared membrane was really ZIF-71, the Fourier transform infrared (FTIR) (Figure S3 in the Supporting Information) spectrum of the sample collected from the surface of the ZIF-71 membrane was tested. The corresponding peaks at 665 cm^{-1} (vibration of C−Cl) and 1053 cm^{-1} (vibration of C−N) matched well with these of the ZIF-71 crystals.[16]

For comparison, we also prepare the ZIF-71 hollow fiber membrane by the secondary growth method. Only discontinuous membrane can be observed (Figure S4 in the Supporting Information), indicating that the controlled contra-diffusion process is very beneficial for fabricating integrated ZIF-71 hollow fiber membranes. Interestingly, we found that the location of the membrane (inner surface or outer surface of the hollow fiber supports) followed the position of the Zn^{2+} reactant. As shown in Figure S5 in the Supporting Information, when the Zn^{2+} reactant was offered in the lumen of the supports, an inner-surface membrane was obtained. But it is very difficult to prepare an integrated inner-surface membrane based on our method because some dispersive ZIF-71 crystals could stack in the lumen. In addition, the outer-surface membranes may be desired because of the higher surface area.

The high affinity of organics to the membrane is very important for the separation of organic solvents. Herein, we measured the contact angles of water and ethanol on the ZIF-71 membrane. For ethanol, only dynamic decrease processes of contact angles can be observed (Figure S6a in the Supporting Information) because ZIF-71 can adsorb ethanol molecules. The static contact angle of water on the membrane is about 92.9° (Figure S6b in the Supporting Information), which is close to the literature data.[18] In addition, the adsorption ability of ZIF-71 crystals was tested by a quartz crystal microbalance technique. As shown in Figure S7 in the Supporting Information, ZIF-71 shows stronger sorption ability for ethanol than water. These results demonstrate that ZIF-71 is highly organophilic and very suitable for pervaporation separation of organic solutions.

Before the pervaporation analysis, the membrane was activated at 100 °C. The thermogravimetric analysis (Figure S8 in the Supporting Information) indicates that the guest molecules in the cages of ZIF-71 had been removed completely.

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The themogravimetric curve also illustrates that ZIF-71 possesses good thermal stability, up to 450 °C. Figure 3

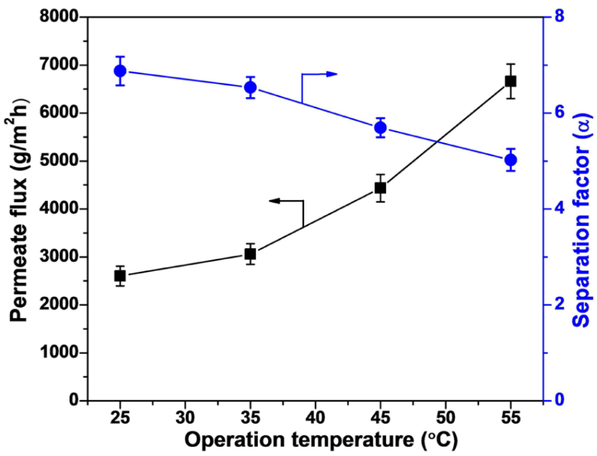

Figure 3. Performance of ZIF-71 membranes for ethanol recovery from 5 wt % ethanol aqueous solution.

shows the performance of ZIF-71 membranes for ethanol recovery from 5 wt % ethanol aqueous solution. With increasing the operation temperature, the permeation flux increases because the driving force is enlarged. In contrast, the separation factor decreases from 6.88 to 5.02 since the sorption ability of ZIF-71 crystals declined. It is worth to note that the permeate flux (2,601 g/m^2 h, at 25 °C) in this work is much larger than the literature results (the permeate flux and separation factor reported by Dong et al. at 25 °C are 332 g/m^2 h and 6.07, respectively[18]). And, the permeate flux and separation factor of the ZIF-71 hollow fiber membrane can reach the average performance of current ethanol-permselective membranes. This inspiring result can attribute to the low resistance of ceramic hollow fiber supports and the thin membrane thickness.

In summary, a hydrophobic ZIF-71 hollow fiber membrane was successfully fabricated by the contra-diffusion method. The as-prepared membrane is of very high integrity and thin. Because of its highly organophilic ability, the ZIF-71/hollow fiber composite membrane exhibited excellent separation performance for the recovery of ethanol. The results demonstrate that ZIF-71 membrane can be expected as potential ethanol-selective membranes for clean biofuel production.

■ ASSOCIATED CONTENT

Supporting Information

Reaction process photos, adsorption and thermogravimetric results of ZIF-71 crystals; XRD pattern, FTIR spectrum, and contact angles of ZIF-71 membranes; SEM images of ZIF-71 membrane prepared by the secondary growth method and inner-surface ZIF-71 membrane; experimental section. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b04991.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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