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Mixed-Matrix Membranes

Simultaneous Spray Self-Assembly of Highly Loaded ZIF-8–PDMS Nanohybrid Membranes Exhibiting Exceptionally High Biobutanol-Permselective Pervaporation**

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Abstract: *The ability to obtain a maximum loading of inorganic nanoparticles while maintaining uniform dispersion in the polymer is the key to the fabrication of mixed-matrix membranes with high pervaporation performance in bioalcohol recovery from aqueous solution. Herein, we report the simultaneous spray self-assembly of a zeolitic imidazolate framework (ZIF)–polymer suspension and a cross-linker/catalyst solution as a method for the fabrication of a well-dispersed ZIF-8–PDMS nanohybrid membrane with an extremely high loading. The ZIF-8–PDMS membrane showed excellent biobutanol-permselective pervaporation performance. When the ZIF-8 loading was increased to 40 wt%, the total flux and separation factor could reach 4846.2 g m*$^{-2}$ *h*$^{-1}$ *and 81.6, respectively, in the recovery of n-butanol from 1.0 wt% aqueous solution (80 °C). This new method is expected to have serious implications for the preparation of defect-free mixed-matrix membranes for many applications.*

Research on new energy is concerned to a great extent with the development of renewable and clean biofuels, such as bioethanol and biobutanol.[1] Biobutanol as a fuel has properties that are superior to those of bioethanol, including higher energy density, lower volatility, and its amenability to the formation of higher-level blends with petroleum.[2] However, butanol production by fermentation is severely limited by inhibition by products, which results in low reaction productivity and a low final concentration of the butanol product (0.5–1 wt%).[3] Additionally, the separation of butanol from the aqueous medium is energy-intensive.[4] The pervaporation technique is considered to be the most promising separation technology because of its energy efficiency, cost effectiveness, and harmlessness to microorganisms as compared with the conventional methods of distillation and extraction.[5] Specifically, the technique of organophilic pervaporation (OPV) coupled with fermentation enables in situ and continuous removal of butanol from fermentation broths and can effectively enhance the conversion rate and lead to high concentrations of butanol.[6]

The successful application of the OPV process for the recovery of organic compounds from aqueous solution at both laboratory and industrial scales depends significantly on the appropriate chemical, mechanical, and permeation properties of the membrane.[7] However, developments in polymeric membrane materials have apparently reached a limit in the trade-off between permeability and selectivity.[4a,7c] For example, the modified poly(vinylidene difluoride) membrane reported by Srinivasan et al. exhibited high flux (4126 g m^{-2} h^{-1}) but poor selectivity (6.4) in the separation of a 7.5 wt% *n*-butanol/water feed solution at 50 °C.[8] In contrast, a trilayer polydimethylsiloxane (PDMS) composite membrane showed high selectivity (34) but low flux (95 g m^{-2} h^{-1}) at 37 °C in the separation of a 1.0 wt% *n*-butanol/water feed solution.[9] Although some inorganic membranes show high performance relative to that of polymeric membranes,[10] the high fabrication costs[11] and the lack of maturity of the preparation method prevent their development toward commercial distribution.[12]

To overcome the limitations of these two types of membranes, several research groups have investigated the potential of mixed-matrix membranes (MMMs) with porous fillers, including silicalite, zeolite, silica, carbonaceous particles, and metal–organic frameworks (MOFs; e.g., zeolitic imidazolate frameworks (ZIFs)), dispersed in the polymer matrix.[9,13] MMMs are expected to combine the potential advantages in the separation performance of both inorganic and polymeric membranes. They therefore figure in the developing trend in membrane separation technology.[14]

One representative study on MMMs examined the ZIF-8–polymethylphenylsiloxane (PMPS) membrane,[15] which exhibited an optimal selectivity of 40.1 and productivity of 6400 g m^{-2} h^{-1} in the recovery of isobutanol (1.0 wt%) from water. However, filler dispersion is poor even at a ZIF-8 loading of 10% (w/w), thereby limiting further enhancement of the membrane performance in biobutanol separation.

In light of the aforementioned analysis, it is apparent that it is difficult to obtain a maximum loading of ZIF-8 particles while maintaining uniform dispersion to improve pervaporation performance in biobutanol recovery from aqueous solution. Herein, we report the use of a simultaneous spray self-assembly technique to fabricate a ZIF-8–polydimethylsiloxane (PDMS) nanohybrid composite membrane on sheet

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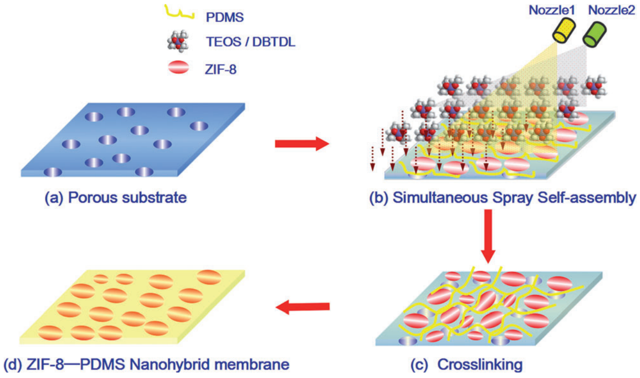
polysulfone (PS) substrates with the aim of maximizing the dispersion and loading of ZIF-8 particles. The generation of an ultrathin nanohybrid selective layer by use of the improved automated simultaneous spray system was expected. The as-synthesized high-loading ZIF-8–PDMS membrane was therefore expected to show better biobutanol-pervaporation performance. Factors leading to the high loading and high performance of the ZIF-8–PDMS membrane were studied in detail.

The membranes were prepared with an improved automated spray system that was fabricated in-house (see details in Scheme S1 of the Supporting Information); the process of membrane formation is shown in Scheme 1. Thus, the ZIF-8–PDMS suspension and a solution of the cross-linking agent tetraethyl orthosilicate (TEOS) and the catalyst dibutyltin dilaurate (DBTDL) were poured separately into two self-stirring pressure barrels and simultaneously sprayed onto a PS substrate. To analyze the dispersion status of the as-synthesized ZIF-8–PDMS membrane with a changing ZIF-8 loading, we characterized the morphologies of the membrane surface by scanning electron microscopy (SEM). For comparison, hybrid membranes were also prepared in parallel through the doctor blading method (see Scheme S2). ZIF-8 nanoparticles (see Figures S1–S3) of the doctor-bladed membrane evidently aggregated even at relatively low loadings (10 and 20 %, w/w; see Figure S4 b,c). As the ZIF-8 loading increased, there was more serious aggregation of ZIF-8 crystals into grapelike clusters (see Figure S4 d,e). In contrast, SEM images of the sprayed membrane clearly showed that ZIF-8 crystals were well-dispersed in the PDMS cross-linking layer at relatively low loadings (10–30 %, w/w; Figure 1 a–c) and even at an extremely high loading (40 %, w/w; Figure 1 d). X-ray diffraction (XRD) confirmed that ZIF-8 nanoparticles penetrated the PDMS layer, as diffraction peaks related to ZIF-8 were present in the patterns of the ZIF-8–PDMS membrane (Figure 1 e).



Scheme 1. Formation of the ZIF-8–PDMS nanohybrid composite membrane by the simultaneous spray self-assembly technique.

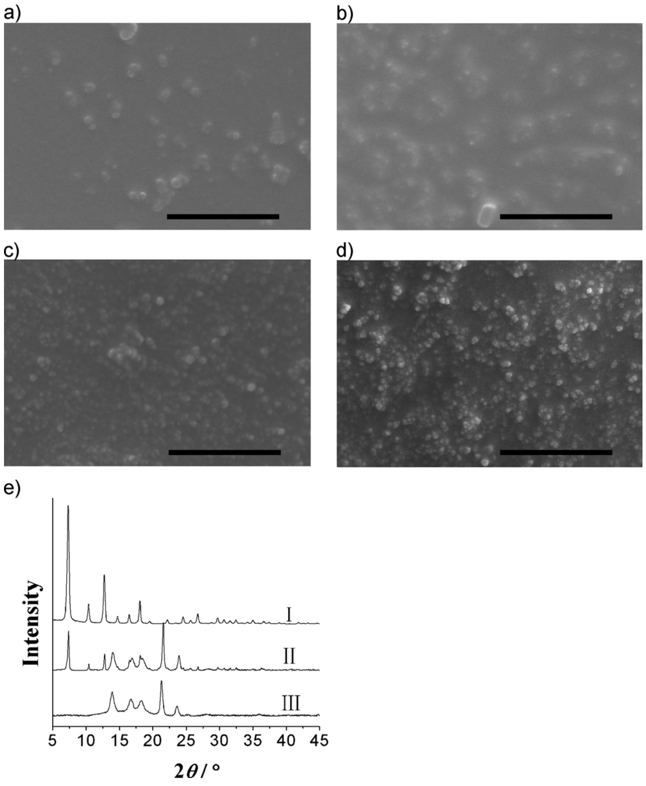


Figure 1. Surface SEM images of ZIF-8–PDMS membranes fabricated by the spray self-assembly technique at ZIF-8 loadings of a) 10 % (w/w), b) 20 % (w/w), c) 30 % (w/w), and d) 40 % (w/w). e) XRD patterns of ZIF-8 nanoparticles (I), a pure PDMS membrane (III), and a ZIF-8–PDMS membrane (40 %, w/w; II). Scale bars: 1 μm.

There are two main reasons for the extremely high loading and homogenous dispersion of ZIF-8 nanoparticles in the PDMS cross-linking layer obtained by the simultaneous spray self-assembly technique. Since the PDMS suspension with ZIF-8 nanoparticles was sprayed onto the PS membrane surface by mechanical atomization, the ZIF-8 nanoparticles were dispersed uniformly on the PS membrane surface, and they were separated individually by the PDMS chains. Upon spraying of the TEOS–DBTDL solution, cross-linking reactions occurred on the PS membrane surface. As a result, ZIF-8 nanoparticles were further surrounded individually by PDMS chains by the confinement effect. Additionally, self-stirring in the pressure barrels was maintained at a stable state, which resulted in a uniform dispersion of ZIF-8 nanoparticles in the PDMS solution and thereby prevented nanoparticle aggregation during spraying by the improved automated spray system. Therefore, ZIF-8 in the PDMS membrane was uniformly dispersed after further cross-linking and treatment, regardless of the ZIF-8 loading.

The pervaporation performance in the recovery of *n*-butanol from a 1.0 wt % aqueous solution was studied by sealing the as-synthesized ZIF-8–PDMS membrane in a module that was fabricated in-house (see Scheme S3). The spray-assembled ZIF-8–PDMS membrane in this study exhibited the best overall pervaporation performance when compared with other previously reported membranes (Figure 2 a; see also Table S1 in the Supporting Information). The optimal pervaporation performance of the ZIF-8–PDMS membrane with an extremely high loading of ZIF-8 (40 %, w/w) afforded a relatively high total flux (4846.2 $\mathrm{g\,m^{-2}\,h^{-1}}$) and a higher separation factor (81.6, which is almost twice that

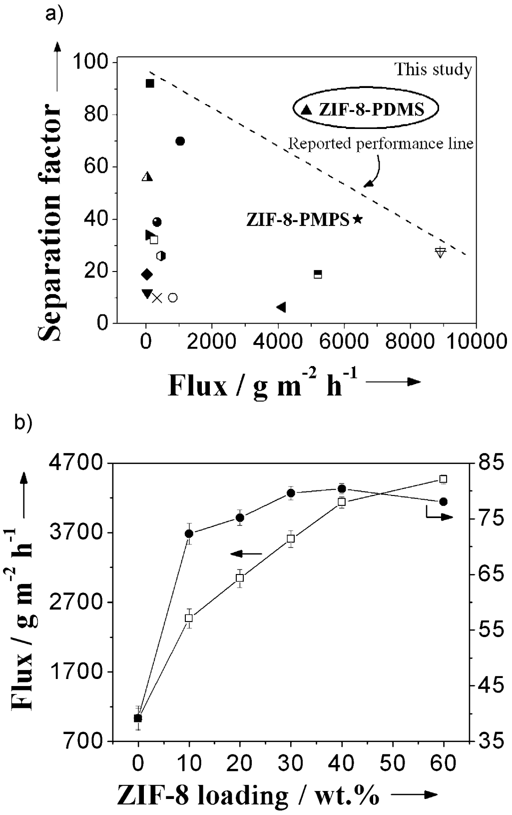


Figure 2. a) Pervaporation performance in the recovery of butanol from aqueous solutions as reported previously and in our study. b) Effect of the ZIF-8 loading on the performance of ZIF-8–PDMS membranes in the separation of 1.0 wt% aqueous *n*-butanol at 60 °C. Error estimates varied from 2.5 to 9.8% for the flux and from 0.7 to 9.5% for the separation factor.

of the ZIF-8–PMPS membrane) at a feed temperature of 80 °C. These results suggest that when the feed side of the membrane is exposed to a 1.0 wt% solution of *n*-butanol from a typical fermentation, around 45 wt% of *n*-butanol could be obtained on the permeate side.

Both the permeation flux and the separation factor of the ZIF-8–PDMS membranes were far higher than those of a pure PDMS membrane (Figure 2b). More importantly, there was a simultaneous significant increase in the flux and separation factor as the ZIF-8 loading in the ZIF-8–PDMS membrane was increased up to 40 wt%. This trend can be explained by the stronger affinity of the membrane for *n*-butanol at a higher uniform ZIF-8 loading, as demonstrated by contact-angle measurement and a solvent-adsorption experiment (see Figures S5 and S6). This property offers the possibility of achieving very high separation performance. The separation factor, however, decreased with a further increase in the ZIF-8 loading (60%, w/w). This anomaly could be attributed to severe agglomeration of ZIF-8 (see Figure S7). Furthermore, it is well-known that the membrane flux is proportional to the thickness of the selective layer. The thickness of the top selective layer (Figure 3a) was only about 800 nm, which is far thinner than that of a membrane fabricated by the traditional doctor blading method, which had a thickness of 35 μm (see Figure S4a). The selective-layer thickness in this study was thinner than that of other reported butanol-permselective composite membranes (Figure 3b). The ultrathin selective layer increases the permeation flux because of its lower diffusional resistance.[16] Furthermore, the thickness of the selective layer could be tuned readily within a nanoscale range by adjusting the spraying cycles (see Figure S8). The permeation flux and separation factor increased simultaneously with an increasing feed temperature (see Figure S9), thus also demonstrating the anti-tradeoff effect of the ZIF-8–PDMS membranes.

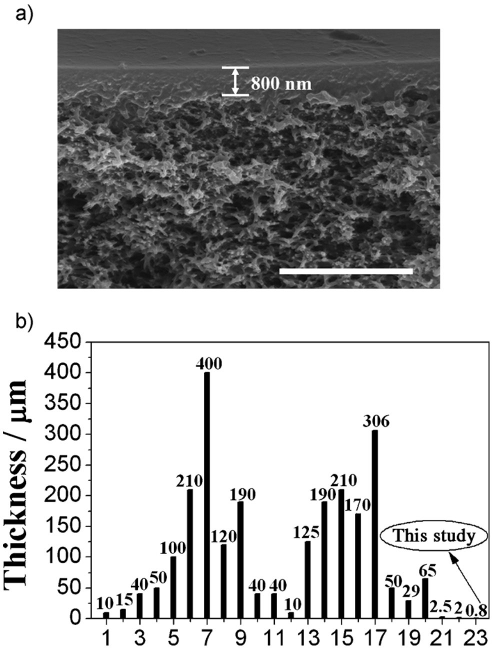


Figure 3. a) Cross-sectional SEM image of the ZIF-8–PDMS membrane (40%, w/w) prepared through two cycles of the spray self-assembly technique. Scale bar: 5 μm. b) Thickness of the selective layer of known butanol-permeative membranes (see Table S1).

The ZIF-8 structures were flexible enough to allow the passage of molecules such as butanol, which is larger than the crystallographically derived aperture size.[17] This structural flexibility contributes to the adsorption selectivity of the ZIF-8 hybrid membrane. It also facilitates the permselective pervaporation of butanol, as the adsorption selectivity is a controlled factor in the pervaporation process, which is governed by solution diffusion.[18] A high loading of ZIF-8 nanoparticles in the PDMS cross-linking layer can create more preferential pathways for *n*-butanol molecules by virtue of their ultrahigh adsorption selectivity. But how could *n*-butanol molecules rather than water molecules preferably pass through the membrane with an extremely high loading of ZIF-8–PDMS? It is very difficult for MMMs to reach the ideal morphology, which has no defects and no distortion at the filler–polymer interface.[7c,19] The ZIF-8–PDMS membrane is no exception, although ZIF-8 materials are more compatible with the polymeric phase because of the imidazolate rings in their framework.[20] There may be three routes through which the feed solution penetrates the selective layer (Figure 4b): through the PDMS dense layer, the ZIF-8–PDMS interface (gaps), and the inner channels of the ZIF-8

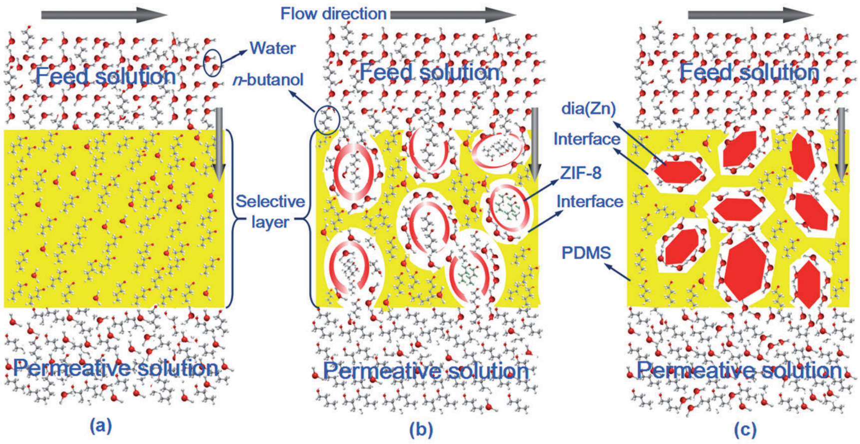


Figure 4. Transport process of permeating components in the selective layer of a) a pure PDMS membrane, b) the ZIF-8–PDMS nanohybrid membrane, and c) the dia(Zn)–PDMS membrane.

nanoparticles. The PDMS dense layer and the inner channels of the ZIF-8 nanoparticles are considered as butanol-permselective paths because of their organophilicity and hydrophobicity.[21] The interface is considered to be a water-permselective path because the water molecule has a kinetic diameter that is smaller (2.96 Å) than that of *n*-butanol (5.05 Å), and it has a higher diffusion rate.[20b] In the pervaporation process, the butanol/water mixture preferentially diffuses through the inner channels of ZIF-8 nanoparticles and gaps because their diffusional resistance is lower than that of the dense and nonporous PDMS layer, thus greatly improving the permeation flux. Therefore, the permeation flux increases with increasing ZIF-8 loading. Although the separation factor decreases with increasing ZIF-8 loading because of the greater number of gaps produced in the selective layer, higher loadings increase the probability of the diffusion of butanol molecules into the channels. Therefore, the butanol permselectivity and separation factor in this layer are high.

The surface groups and elements of dia(Zn) (dia framework, Zn(mim)$_2$, mim = 2-methylimidazolate) are the same as those of ZIF-8, but dia(Zn) has no pores, as demonstrated by energy-dispersive spectroscopy (EDS), Fourier transform infrared (FTIR) spectroscopy, and gas sorption analysis (see Figures S1c and S10–S12). This lack of pores implies that water and *n*-butanol molecules can not move into the framework, and that the butanol/water mixture penetrates the selective layer through two paths: the PDMS dense layer and dia(Zn)–PDMS interface (Figure 4c). For comparison, we synthesized dia(Zn)–PDMS membranes by the same procedure. The permeation flux clearly increased and the separation factor decreased with increasing dia(Zn) loading (see Figure S13). This result indicates that the gaps between dia(Zn) and PDMS comprised the water-permselective path. This finding also confirms that the adsorption selectivity and framework flexibility of the ZIF-8 nanoparticles significantly contributes to the selective permeation of *n*-butanol molecules.[17a]

To ensure the accuracy of the results and to eliminate the interference of particle size, we synthesized microsized ZIF-8 particles (see Figure S1b) that had dimensions similar to those of dia(Zn). We also prepared a ZIF-8–PDMS membrane from the microsized particles by the same procedure. The microsized-ZIF-8–PDMS membrane showed trends in the flux and separation factor (see Figure S14) that were similar to those observed with the nanosized-ZIF-8–PDMS membrane. Its performance, however, was slightly poorer than that of the nanosized-ZIF-8–PDMS membrane because of the smaller contact area between the particles and *n*-butanol.

In conclusion, ZIF-8–PDMS membranes with a high ZIF-8 loading and an ultrathin selective layer were successfully fabricated by a spray self-assembly technique that is simpler and more reproducible than other methods. The dispersion uniformity of the fillers and their compatibility always had an important effect on the pervaporation performance of the membranes. The ZIF-8–PDMS membrane with a 40% (w/w) ZIF-8 loading showed a high total flux (4846.2 $\mathrm{g\,m^{-2}\,h^{-1}}$) and a separation factor of 81.6 at a feed temperature of 80 °C. It exhibited an optimal overall pervaporation performance as compared with that of other reported membranes. We found that butanol molecules mainly pass through the inner channel of ZIF-8, whereas water molecules mainly pass through the interface between PDMS and ZIF-8 particles in such ZIF-8–PDMS membranes with an extremely high loading. In view of the versatile architectures and customizable chemical functionalities of MOF materials, as well as the simplicity, speed, and reproducibility of the spray self-assembly technique, this technology may contribute to the preparation of various MOF hybrid membranes and extend the use of these membranes to industrial applications.

Experimental Section

PS ultrafiltration sheet membranes (nominal molecular weight cutoff: 20000; Sepro Membranes) were used as supports. After pretreatment with a 30 wt% aqueous ethanol solution and ultrapure water, the membrane was cut into flat circular plates, which were then fixed perpendicularly onto the substrate. The as-synthesized ZIF-8 nanoparticles were dispersed in *n*-heptane (AR grade; Beijing Chemical Works) by ultrasonic treatment with stirring for 2 h, and PDMS was then added to the mixture. The resulting mixture was stirred for 1 h to give a homogeneous polymer suspension. The PDMS content in the suspension was 10 wt%, and the weight ratio of ZIF-8 to PDMS was 10 to 60%. The cross-linking agent TEOS (1 wt%) and the catalyst dibutyltin dilaurate (DBTDL; 0.05 wt%) were dissolved in *n*-heptane, and the resulting mixture was stirred at room temperature for 1 h. To prepare a homogeneous and defect-free pervaporation hybrid composite membrane, the PDMS–ZIF-8 suspension and the TEOS–DBTDL solution were repeatedly sprayed onto a PS substrate. The spraying could be controlled by using a programmable logic controller system (PLC). The operation parameters, namely, the spraying rate, standing interval, distance between the substrate and nozzle, and rotation speed of the substrate were set at 2–3 mL s^{-1}, 1 min, 45 cm, and 100 rpm, respectively. After spraying, the samples were allowed to stand for 1 day to remove the remaining solvent. Finally, the samples were placed in a vacuum oven set at 80 °C for 8 h to fully cross-link the PDMS solution.

More experimental and characterization details (e.g. gas sorption analysis, SEM, EDS, XRD, FTIR spectroscopy, and pervaporation measurements) are described in the Supporting Information.

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