Vesicles-shaped MOF-based mixed matrix membranes with intensified interfacial affinity and CO₂ transport freeway

Rui Ding a, Yan Dai a,c, Wenji Zheng a,b, *, Xiangcun Li a, Xiaoming Yan b, Yi Liu a, Xuehua Ruan b, Shaojie Li b, Xiaochen Yang b, Kai Yang b, Gaohong He a,b,

a State Key Laboratory of Fine Chemicals, R&D Center of Membrane Science and Technology, School of Chemical Engineering, Dalian University of Technology, Dalian 116023, PR China
b State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Panjin 124221, PR China

* Corresponding authors at: State Key Laboratory of Fine Chemicals, R&D Center of Membrane Science and Technology, School of Chemical Engineering, Dalian University of Technology, Dalian 116023, PR China.
E-mail addresses: zhengwenji@dlut.edu.cn (W. Zheng), hgaohong@dlut.edu.cn (G. He).

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ABSTRACT
The trade-off between gas permeability and selectivity represents a huge challenge for membrane separation. In this work, we design unique polystyrene-acrylate (PSA) modified hollow ZIF-8 (PHZ) nanospheres via a facile hard template-incomplete etching strategy as fillers for mixed matrix membranes (MMMs). In the vesicles shaped PHZ, the hollow core builds a low-resistance CO₂ transport freeway, leading to improved CO₂ permeability. Meanwhile, the outside PSA layer intensifies the interface affinity between ZIF-8 and Pebax through molecular chains entanglements and hydrogen bonding, enhancing membrane selectivity. Through controlling the PSA etching process, both the hollow core with tunable size and the outside PSA layer with adjustable thickness are achieved. The 10 wt% PHZ-2/Pebax MMMs present the best performance with a CO₂ permeability of 172.4 Barrer and CO₂/N₂ selectivity of 87.9. The higher CO₂/N₂ selectivity proves that the PSA layer on the PHZ has better compatibility with Pebax. The higher CO₂ permeability is attributed to the low-resistance hollow core. The gas separation performance of PHZ-based MMMs not only well exceeded the 2008 Robeson upper-bound line but also was superior to those of other published MOF-based MMMs. The concept of vesicle-shaped PHZ paves a way to concurrently enhance both the gas permeability and selectivity of MMMs.

1. Introduction
The capture and storage of CO₂, a major greenhouse gas as well as an important carbon resource, has been urgently required for environmental protection and sustainable development. As a new technology combining the advantages of polymer membrane and inorganic membrane, mixed matrix membranes (MMMs) have been widely developed for the CO₂ capture and much more appealing results have been acquired over the past years [1–3]. Particularly, metal-organic framework (MOF)-based mixed matrix membranes have been demonstrated as a prospective way to capture CO₂, and been expected to overcome Robeson’s upper bound due to the abundant micropores and organic linkers in MOFs [4,5]. However, poor interfacial compatibility between MOFs and polymer matrix remains a critical issue resulting in CO₂ separation performance far from the ideal situation [6,7].

Recently great efforts have been devoted to effective interface engineering between MOFs and polymer, such as filler geometry [8,9], in-situ synthesis [10] and surface modification [11–13]. Benefiting from operability and universality, surface modification strategy, including functional group modification, hydrocarbyl chain modification, and polymer modification, has been extensively studied. In general, functional groups, such as amino, carboxyl or hydroxyl, etc. are used to modify MOFs to improve the affinity between MOFs and polymer [14] or to cross-link with the matrix to eliminate interfacial defects [15]. Moreover, hydrocarbyl chains including alkyl and aromatic on MOFs could form hydrogen bonds or π–π stacking with polymer to improve interfacial compatibility. So far various polymers, such as PI and PEI, have been used to decorate MOFs to modify the interface. Besides the electrostatic and hydrogen bonding interaction between MOFs and membrane matrix [16], unique segment interactions between the
modified polymer and membrane matrix also enable to enhance the interface compatibility [17]. However, in most cases, the gas selectivity in most reported MMMs is greatly improved at the expense of reducing gas permeability. For further improving the permeability, MOFs with core-shell [18] and hollow structure [19] were introduced into MMMs to provide low-resistance transport pathway for gas molecules. Nevertheless, as mentioned above, the increase in permeability usually sacrifices some selectivity.

Aiming at concurrently improving the gas permeability and selectivity, based on the goal of one-bullet-two-objects, herein we present a facile hard template-incomplete etching strategy to synthesize a special polystyrene-acrylate (PSA) modified hollow ZIF-8 (PHZ) in one step. This unique structure not only intensifies the interface affinity, but also provides a low-resistance CO\(_2\) transport channel. As illustrated in Scheme S1, PSA is first used as a hard template to allow ZIF-8 to grow on its outer surface. Through controlling the PSA etching process, hollow core with a tunable size is obtained. Meanwhile, residual PSA molecules penetrate through the interval space among ZIF-8 nanoparticles and adhere to hollow ZIF-8 nanospheres to form an outer PSA coating layer. With this method the thickness of the coating layer can be easily controlled by adjusting the PSA etching time. The gas separation mechanism of PHZ/MMM is shown in Scheme 1. With the help of functional PSA layer, the PHZ can be readily dispersed into polymer matrix (shown in Scheme 1 left). Different from the ZIF-8/Pebax MMM with interfacial defects (white parts), PSA molecular chains outside PHZ entangle with Pebax (red parts and enlarged view) and the hydrogen bonding between Pebax and PHZ is formed (imine groups and carboxyl groups, carbonyl groups and carboxyl groups, enlarged view). The hydrogen bonding can reinforce the interfacial compatibility between PHZ and Pebax, resulting in less interface defects and thus considerable improvements in selectivity. In addition, benefiting from the hollow structure, the effective gas mass transfer distance \(D_{\text{E}} = a + b + c\) of PHZ based MMMs is shorter than the normal mass transfer distance \(D_{\text{N}}\) of ZIF-8 based MMMs, resulting in higher gas permeability of PHZ-based MMM. As a result, the synergistic effect of PSA modification and hollow structure leads to simultaneous improvements in gas selectivity and permeability.

2. Experimental

2.1. Materials

Commercial Pebax MH 1657 was used as the polymer for preparation of MMMs. Sodium dodecyl sulfate (SDS, C\(_{12}\)H\(_{25}\)SO\(_4\)Na, 99%), potassium persulfate (KPS, K\(_2\)S\(_2\)O\(_8\), 99%), styrene (C\(_8\)H\(_8\), 99.5%), acrylic acid (C\(_3\)H\(_4\)O\(_2\), 99.5%), methanol (CH\(_3\)OH, 99%), sodium bicarbonate (NaHCO\(_3\), 98%) and N,N-dimethylformamide (DMF, C\(_3\)H\(_7\)NO, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Zinc nitrate hexahydrate (Zn(NO\(_3\))\(_2\)⋅6H\(_2\)O, 98%), 2-methylimidazole (Hmim, C\(_4\)H\(_6\)N\(_2\), 98%) were purchased from Aladdin. All solvents and chemicals were used without further purification.

2.2. Synthesis of carboxylation polystyrene (PSA) nanoparticles

Nanosized PSA particles were synthesized via an emulsion polymerization method as published with some modification [20]. Typically, 100 mL deionized water was added into a three-necked flask and followed by addition of 24.8 mg sodium dodecyl sulfate, 240 mg sodium bicarbonate and 100 mg potassium persulfate. Then, 8 mL styrene and 2 mL acrylic acid were poured into the aqueous solution. The sample were kept stirring for 4 h at 80 °C under N\(_2\) atmosphere. The obtained samples were centrifuged and washed with ethanol and deionized water for several times.

2.3. Synthesis of PSA modified hollow ZIF-8 nanospheres

Generally, 120 mg of zinc nitrate hexahydrate and 66.4 mg of 2-methylimidazole were dissolved in 64 mL of methanol. Then, 176 mg PSA were added into the precursor solution with ultra-sonication for 5 min. The samples were kept in an oil bath at 70 °C for 30 min and

\[D_{\text{E}}: \text{Effective gas mass transfer distance (}D_{\text{E}} = a + b + c\)]

\[D_{\text{N}}: \text{Normal gas mass transfer distance (}D_{\text{N}}\)
subsequently centrifuged to collect the PSA@ZIF-8 particles. Then the PSA@ZIF-8 samples were dissolved in 200 mL DMF at 25 °C for a controlled time to remove the PSA core incompletely, and the final PHZ nanospheres were collected by centrifugation at 9000 rpm for 10 min. Then the obtained PHZ nanoparticles were washed with ethanol and water several times and dispersed in ethanol. In this work, we prepared three kind of PHZ with different PSA modification by controlling the etching time (PHZ-1: 2 days, PHZ-2: 8 days and PHZ-3: 16 days). Meanwhile, unmodified ZIF-8 without the addition of PSA was synthesized in the same way for comparison.

2.4. Fabrication of MMMs

The MMMs were fabricated by solution casting [21,22]. Firstly, the Pebax MH 1657 solution (3.0 wt%) was prepared as the common method. Then, a certain amount of PHZ were dispersed in the Pebax solution and sonicated to remove the bubbles of the casting solution. Then the PHZ/Pebax solution was poured into petri dishes and the membrane was obtained after drying the solution at 40 °C for 24 h. The membranes were putted at the vacuum oven for 24 h to remove residual solvents.

The PHZ loading is defined as subsequent equation:

\[
\text{PHZ loading (wt%)} = \frac{m_{\text{PHZ}}}{m_{\text{Pebax}} + m_{\text{PHZ}}} \times 100\%
\]

In this work, the loading of PHZ in MMMs ranged from 0 to 15 wt%.

2.5. Characterization

The size and the morphology of PHZ and the dispersion of the filler in MMMs were characterized with Nova Nano SEM 450 scanning electron microscopy (SEM) at 20 kV. The cross sections of MMMs were prepared under liquid N₂. Transmission electron microscopy (TEM) was used to characterize the hollow structure of ZIF-8. X-ray diffraction (XRD) data of all materials and films were obtained from 5 to 40° at a scanning rate of 5° from an XRD-7000S X-ray diffractometer (60 kV and 80 mA). Nitrogen adsorption-desorption isotherms were used to characterize the surface area of PHZ and measured at −196 °C using a porosity analyzer.

Fig. 1. XRD patterns (a), and FTIR (b) of PSA, PSA@ZIF-8 and PHZ-2 nanospheres.

Fig. 2. SEM, TEM and EDS images of PSA (a, d), PSA@ZIF-8 (b, e) and PHZ-2 (c, f).
Samples were heated in N$_2$ flow from 30 °C to 600 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Characterizations of PHZ nanospheres

XRD patterns of PSA@ZIF-8 and PHZ are shown in Figs. 1a and S1. It can be seen that all samples exhibit a diffraction peak at 19.4°, which originates from the PSA polymer [23]. This result indicates the presence of residual PSA in all PHZ samples. It is obvious that PHZ-2 shows the same diffraction peaks with ZIF-8, confirming that ZIF-8 is synthesized successfully in PHZ-2 and retains the crystallinity [24–26]. The same conclusion can be drawn from PHZ-3 (Fig. S1). However, no diffraction peak for ZIF-8 is observed in PHZ-1 (Fig. S1), which can be attributed to the fact that specific diffraction peaks of ZIF-8 are masked by PSA residuals with slight etching of PHZ-1.

FTIR spectra of ZIF-8, PSA, PSA@ZIF-8 and PHZ-2 are recorded in Fig. 1b. It is noted that PSA, PSA@ZIF-8 and PHZ-2 show different FTIR spectra with ZIF-8 due to the existence of PSA. Particularly, –CH stretching vibration peaks on the benzene ring appear in 3025, 3059 and 3082 cm$^{-1}$; the new peak at 3400 cm$^{-1}$ is derived from the –OH; the other peak at 1720 cm$^{-1}$ represents the stretching vibration peak of C=O. Besides, there is no peak in 1639 cm$^{-1}$, revealing that acrylic acid is polymerized with styrene and –COOH is introduced into PSA successfully [22,27]. It is worth noting that the vibration peak of Zn-N at 420 cm$^{-1}$ appears in PHZ-2 and PHZ-3, but not in PHZ-1 and PSA@ZIF-8 (Figs. 1b and S2), which is similar to the XRD result. It is probably that the Zn-N peak in PHZ-1 and PSA@ZIF-8 is masked by the PSA.

The thermal analysis curve of PHZ conducted under N$_2$ flow from 30 °C to 600 °C [28,29] on the surface of PSA. Meanwhile, the decomposition temperature of PHZ slightly increases from 420 °C (PHZ-1) to 430 °C (PHZ-3) accompanying with concurrent increase of residual weight which is attributed to the decrease of PSA and increase of ZIF-8 in PHZ with increasing the etching time. Anyway, the above results prove that the PSA content in PHZ can be controlled through the etching time.

The size, morphology and hollow structure of PSA and PHZ-2 are characterized by SEM and TEM (shown in Fig. 2). To confirm the PSA etching process and the formed PHZ structure further, SEM, TEM images and EDS mappings of all PHZ samples are shown in Fig. S4. Fig. 2a implies that spherical PSA nanospheres have uniform sizes of about 100 nm with smooth surface. After ZIF-8 growth, the PSA surface becomes rough and the size increases to 110 nm (shown in Fig. 2b), indicating the successful coating of ZIF-8 shell on the surface of PSA. As shown in Figs. 2c and S4a–c, compared with PSA@ZIF-8, all PHZ samples exhibit smooth surface, and ZIF-8 nanoparticles on PSA nanospheres surface disappear due to the etching in DMF. Meanwhile, the size of all PHZ samples becomes larger than that of PSA@ZIF-8. Increasing the etching time leads to increase of the size of PHZ from 114 nm to 132 nm (Fig. S4a–c). Therefore, it is reasonable to conjecture the PSA dissolution process as following. DMF transports through both the intervals among ZIF-8 nanoparticles and the micropores of ZIF-8 into the PSA core, resulting in the PSA core swell and dissolved in DMF, then the dissolved PSA molecules penetrate through the intervals among ZIF-8 nanoparticles into the DMF solvent. The gradually increased hollow size of PHZ with etching time from the TEM results in Fig. S4 also verified this. During the PSA molecules transport back into the DMF solvent, due to the interaction between the –COOH of PSA and the Zn$^{2+}$ of ZIF-8, PSA molecules are adsorbed on the ZIF-8 surface, and they are more difficult to swell and dissolve again into DMF solvent. Consequently, hollow ZIF-8 nanosphere with PSA coating layer is formed.

As shown in Figs. 2f and S4d–f, the hollow structure of PHZ is well presented. The PHZ size is enlarged in comparison with PSA@ZIF-8, and the size shows an increase with increasing the etching time, which is consistent with SEM results. It is clearly seen that all PHZ samples show
the same morphology and vesicle shape and the hollow size can be adjusted from 42 nm (PHZ-1) to 91 nm (PHZ-3) by controlling the etching time (Fig. S4d-f and Table S1). Specially, the hollow size of PHZ-3 is close to that of PSA, revealing that PHZ-3 is almost completely etched. Insets in Figs. 2d-f and S4d-f are EDS elemental mappings (Zn and O) of PSA@ZIF-8 and PHZ. The Zn element (green) confirms the existence of ZIF-8, and the O element (red) belongs to the PSA (–COOH). The inset in Fig. 2d shows the large amount of O elements existing in PSA, while lots of Zn elements (green) are observed in the inset in Fig. 2e, indicating the coating of ZIF-8 on PSA. Meanwhile, scattered O element (red) also appears through the whole sphere, which may be caused by the certain depth of EDX irradiation. On the contrary, it is observed that one distinct layer of red O element spreads the outside surface for the three kinds of PHZ samples (the inset in Fig. S4d-f), indicating that PSA template molecules begin to dissolve from the core center, penetrate outside through the interval space among ZIF-8 nanoparticles, and finally adhere on the surface of ZIF-8 to form a PSA coating layer [30,31].

The etching process is further confirmed by etching photographs (Fig. S5). It illustrates that pure PSA dissolves rapidly in DMF (<1 s) and the solution becomes clear. However, for PSA@ZIF-8 nanospheres, the etching becomes slower and the solution becomes cloudy, indicating that the coating ZIF-8 blocks and slows PSA molecules dissolving in DMF. The PSA substrate retained by the incomplete etching provides an anchoring effect on the dissolved PSA segments, meanwhile, Zn2+ in ZIF-8 also interacts with the carboxyl group in the PSA segments, inducing adherents of some dissolved PSA segments on the surface of ZIF-8. Besides, thickness of the coating PSA layer (Table S1) increases from 3.1 nm (PHZ-1) to 11.9 nm (PHZ-3) with the increase of the etching time, demonstrating that more PSA molecules are adsorbed on ZIF-8 surface.

The pore structure of PHZ and ZIF-8 are characterized by nitrogen adsorption-desorption isotherms (shown in Fig. S6). ZIF-8 shows type I isotherm curve, indicating the microporous nature of ZIF-8 [32]. For the PHZ-1 and PHZ-2, there are no obvious adsorption in low relative pressure (<0.1), which is due to ZIF-8 channel blocking by residual PSA. With the increase of the etching time, PHZ-3 shows a higher adsorption than PHZ-1 and PHZ-2 at the low relative pressure, owing to the reduced PSA content and regenerated pores in PHZ-3 caused by long-time etching.

3.2. PHZ/Pebax MMMs

To explore the potential of PHZ nanospheres in CO2 separation, PHZ/Pebax-based MMMs are further prepared. Two peaks of Zn (2p) in XPS spectrum (Fig. S7) confirm the successful incorporation of PHZ into the Pebax matrix. Moreover, from the surface (Fig. S8) and cross-section SEM images (Fig. 3) and the inserted EDS pattern of PHZ-2/Pebax MMMs, the PHZ-2 nanospheres distribute uniformly in the Pebax matrix, and no obvious interface defects are observed, confirming that defect-free MMMs have been successfully prepared. The cross-section image in Fig. 3d illustrates that significant particle agglomeration appears in MMMs with 15 wt% PHZ-2 loading. However, there is still no visible interface defect in the PHZ-2/Pebax MMMs, revealing excellent compatibility between the PHZ and polymer.

3.3. Gas permeability properties

Fig. 4 represents the CO2 permeability and CO2/N2 selectivity of MMMs with different fillers at 10 wt% loading (Fig. 4a) and PHZ-2/Pebax MMMs with different PHZ-2 loading (Fig. 4b). As shown in Fig. 4a, it is observed that PHZ-2/Pebax MMMs exhibit both higher CO2 permeability and CO2/N2 selectivity. The CO2 permeability of all kinds of MMMs are higher than that of pure Pebax membrane, which is attributed to the fact that incorporated fillers destroy the packing of polymer segments and therefore, improve the free volume. The CO2/N2 selectivity of PHZ-based MMMs are higher than that of ZIF-8 and PSA@ZIF-8 (without PSA modification)-based MMMs, confirming that the PSA segment outside PHZ provides a better compatibility with Pebax due to entanglements and hydrogen bonding between PSA and Pebax molecular chains [17,33,34]. Meanwhile, PHZ-2/Pebax MMMs also show higher CO2 permeability than ZIF-8 and PSA@ZIF-8 based MMMs. The increased permeability mainly originates from the hollow structure, which effectively reduces the gas transfer resistance [35]. As shown in Fig. 5f, the CO2 permeability of PHZ-based MMMs increases from 123.5 Barrer (PHZ-1) to 188.4 Barrer (PHZ-3), further demonstrating that the increase of hollow size leads to further reduction in the gas transportation resistance. PHZ-3/Pebax MMMs show a drop in CO2/N2 selectivity compared with PHZ-2 and PHZ-1. The reason is probably that the thicker PSA layer on ZIF-8 surface makes PHZ-3 similar with PSA, thus PHZ-3 based MMM shows the similar separation performance with that of PSA/Pebax MMMs (Fig. 4a). Obviously, the gas separation performance of PHZ-based MMMs can be effectively tuned via controlling PSA layer and hollow size.

As shown in Fig. 4b, it is obvious that the CO2 permeability and CO2/N2 selectivity of PHZ-2/Pebax MMMs are higher than those of pure Pebax membrane. The CO2 permeability of PHZ-2/Pebax MMMs increases with the increase of PHZ-2 loading, owing to improved free volume and low gas transfer resistance caused by the hollow structure of PHZ-2. As for the CO2/N2 selectivity, in the case that the PHZ-2 loading is 10 wt%, the selectivity reaches the highest value of 87.9, which is 80% higher than that of pure Pebax membrane. Further increasing the PHZ-2
loading to 15 wt%, however, leads to easy formation of non-selective defects between the interface and agglomeration of the fillers, resulting in decreased CO$_2$/N$_2$ selectivity. Meanwhile, Table S2 presents gas diffusion and solubility coefficients of PHZ-2/Pebax MMMs obtained by time delay method. It is observed that diffusion coefficients of CO$_2$ and N$_2$ increase with the increase of PHZ-2 loading due to the hollow structure of PHZ. Moreover, the D$_{CO2}$/D$_{N2}$ increases while the loading of PHZ-2 reaches to 10 wt%; simultaneously, compared with the D$_{CO2}$/D$_{N2}$, the S$_{CO2}$/S$_{N2}$ shows a slower increase, revealing that the increased selectivity mainly depends on the diffusion selectivity, which should originate from the superior compatibility between PHZ-2 and Pebax as well as the retarded non-selective diffusion. The long-time stability of the obtained MMMs for CO$_2$/N$_2$ separation is shown in Fig. S10, both the CO$_2$ permeability and CO$_2$/N$_2$ selectivity keep almost unchanged, indicating the fine long-term stability of the PHZ based MMMs.

The comparison of CO$_2$/N$_2$ separation performances of PHZ-2/Pebax MMMs under different pressures (1 bar, 5 bar and 9 bar) with other reported MOF-based and Pebax-based MMMs are presented in Robeson upper bound in 2008 (shown in Fig. 5) and listed in Table S3 [36]. It is observed that, compared with the MOF-based and Pebax-based MMMs, the 10 wt% PHZ-2/Pebax-based MMMs at 1 bar possess both acceptable CO$_2$ permeability (172.4 Barrer) and CO$_2$/N$_2$ selectivity (87.9) and well exceeds the 2008 Robeson upper bound. Meanwhile, with the increase of the feed pressure, the CO$_2$ separation performance of PHZ-2/Pebax MMMs steadily increases [9,17,37–70].

4. Conclusion

In our study, PSA modified hollow ZIF-8 nanospheres are synthesized via a hard template-incomplete etching strategy. The hollow structure can reduce the gas mass transfer resistance so that the gas permeability is improved. In addition, there exist residual PSA segments on the surface of PHZ during formation of the hollow structure, which combines PHZ with Pebax tightly and therefore, enhances the compatibility between PHZ and Pebax. At 10 wt% PHZ-2 loading, the permeability of MMMs reaches 172.4 Barrer, which is 118.5% and 16% higher than that of pure Pebax membrane and ZIF-8/Pebax MMMs, respectively. Meanwhile, the selectivity of 10 wt% PHZ-2/Pebax MMMs increases to 87.9, which is 80% and 118.7% higher than that of pure Pebax membrane and ZIF-8/Pebax MMMs, respectively. The superior gas separation performance of PHZ based MMMs not only well exceeds other published MOF-based MMMs but also is far beyond the 2008 Robeson upper bound. The present study presents a new strategy to synthesize hollow MOF nanoparticles with surface modified PSA in one step and therefore, to concurrently improve the gas permeability and selectivity.


[24] Q. Hou, Y. Wu, S. Zhou, Y. Wei, J. Cano, H. Wang, Ultra-tuning of the aperture size in stifferized ZIF-8-Cm frameworks with mixed linker strategy for enhanced CO2/ 


