Membranes

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A Drying-Free, Water-Based Process for Fabricating Mixed-Matrix Membranes with Outstanding Pervaporation Performance

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Abstract: *Despite much progress in the development of mixed matrix membranes (MMMs) for many advanced applications, the synthesis of MMMs without particle agglomeration or phase separation at high nanofiller loadings is still challenging. In this work, we synthesized nanoporous zeolitic imidazole framework (ZIF-8) nanoparticles with a particle size of 60 nm and a pore size of 0.34 nm in water and directly added them into an aqueous solution of the organic polymer poly(vinyl alcohol) (PVA) without an intermediate drying process. This approach led to a high-quality PVA/ZIF-8 MMM with enhanced performance in ethanol dehydration by pervaporation. The permeability of this MMM is three times higher than that of pristine PVA, and the separation factor is nearly nine times larger than that of pristine PVA. The significantly improved separation performance was attributed to the increase in the fractional free volume in the membranes.*

Pervaporation (PV) is an energy-saving and cost-effective process for separating azeotropic mixtures by using a membrane as a barrier material. PV can be applied in several fields, for example, in biomedical technology and for the dehydration of biofuel.[1] The dehydration of water/ethanol mixtures is particularly important for obtaining high-purity ethanol, which has many uses in industry, medicine, and research.[2] To achieve high separation efficiencies, an efficient PV membrane is required. Thus far, PV membranes have been made from either organic polymers or inorganic materials. Hydrophilic organic polymers such as poly(vinyl alcohol) (PVA),[3] chitosan,[4] or cellulose acetate[5] are generally used for pervaporation dehydration owing to their hydrophilicity and facile membrane-forming properties. Among these organic-polymer-based membranes, PVA membranes were the first polymeric membranes to be commercialized (GFT company, 1980).[6]

Despite these pioneering polymer-based membranes, polymer membranes still suffer from several problems, such as weak mechanical strengths and easy swelling after long-term operation, which reduce the separation performance.[7] Furthermore, for most polymer membranes, there is a trade-off between permeability and separation. Inorganic membranes such as zeolites[8] and carbon molecular sieves[9] with higher mechanical stability[10] have been designed to overcome the trade-off problem; however, these materials are fragile, easily form cracks, and are obtained with low reproducibility. Consequently, mixed matrix membranes (MMMs) that combining the benefits of both organic polymers and inorganic particles have been fabricated.[11]

As one of the most commonly used inorganic materials,[12] metal–organic frameworks (MOFs) have a uniform micropore structure, very high pore volumes, and controllable surface functionality. They can thus provide high selectivity by molecular sieving.[13] Among all MOF materials, ZIF-8 is particularly suitable for the separation of water/ethanol mixtures owing to its pore aperture diameter of 0.34 nm,[14] which is between the kinetic diameters of water (0.296 nm) and ethanol (0.40–0.43 nm).[15] However, there are two major challenges for synthesizing ZIF-8-based MMMs, namely 1) dispersing the ZIF-8 particles in polymer matrixes without obvious agglomeration and 2) avoiding the formation of non-selective interfacial voids between the polymers and inorganic particles.[16]

Although several methods have been reported that solve the dispersion problem of inorganic fillers in organic polymer matrices,[17,18] it is still very challenging to synthesize defect-free MMM with nanosized fillers at high loadings. For example, Mahdi and Tan recently found that aggregation occurred with ZIF-8 loaded Matrimid polymers above a loading of 20 wt %.[19] Consequently, increasing the loading while avoiding the aggregation of inorganic fillers in MMMs is still a scientific and practical challenge.[20]

Herein, we describe a drying-free and water-based mixing process to produce PVA/ZIF-8 MMMs with high loadings of ZIF-8 nanoparticles (up to 39 wt %) for pervaporation dehydration. As shown in Scheme 1, to avoid phase separation and hence the aggregation of particles, water-based

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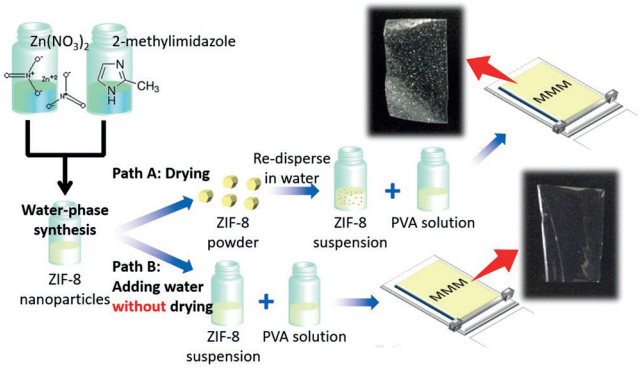

Scheme 1. Preparation of PVA/nano-ZIF-8 MMMs from ZIF-8 suspensions with and without drying.

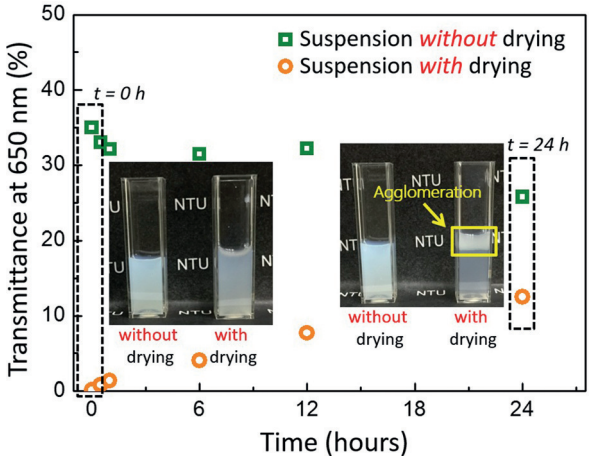

Figure 1. The transmittance at $\lambda = 650$ nm of ZIF-8 suspensions as a function of standing time.

syntheses of ZIF-8 nanoparticles are preferred because the organic polymer PVA is also soluble in water. Water molecules facilitate the distribution of ZIF-8 nanoparticles in the PVA matrix, thus making ZIF-8 nanoparticles compatible with PVA. In contrast to a conventional process that involves the drying and redispersion of ZIF-8 and always results in cracking and phase-separated MMMs (Path A in Scheme 1), our approach does not involve a drying step, and produces a transparent, crack-free MMM with homogeneously dispersed ZIF-8 nanoparticles (Path B in Scheme 1).

The water-based synthesis of ZIF-8 nanoparticles is a modification of a method developed by Lai and coworkers.[21] The size and the specific surface area of the synthesized ZIF-8 particles were estimated to be around 60 nm and 1436 $m^2 g^{-1}$, respectively. The crystal structure and polyhedron morphology of the synthesized ZIF-8 particles were confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM; see the Supporting Information, Figure S1).

To demonstrate the colloidal stability of the solutions containing ZIF-8 nanoparticles, solutions that were prepared with or without drying but contained the same amount of ZIF-8 were monitored with a UV spectrophotometer at $\lambda =$ 650 nm for 24 h. As shown in Figure 1, in the beginning ($t = 0$), the transmittance of the ZIF-8 suspension without drying (Path B) was 35.0 %, which is much higher than that of the suspension obtained with drying (Path A; 0.10 %). The higher transmittance indicates reduced diffraction of incident light, which we propose to be due to the smaller ZIF-8 particle size and better uniformity of the suspension in Path B. Upon increasing the standing time, the transmittance of the suspension with drying (Path A) increased significantly as a result of serious agglomeration. As shown in the inset of Figure 1, most of the ZIF-8 particles aggregated and floated on top of the solution. In contrast, the transmittance of the suspension obtained without drying (Path B) remained almost constant as the standing time was increased, indicating excellent colloidal stability. The good colloidal stability of the ZIF-8 suspension made in the drying-free process (Path B) is a critical factor for fabricating a uniform, crack-free, transparent MMM.

To study the surface properties and morphology of the fabricated PVA/ZIF-8 MMMs, we examined the surface and cross-section of the PVA/ZIF-8 MMM by SEM and EDX (EDX = energy-dispersive X-ray sepctroscopy). As shown in Figures S2 and S3, the PVA/ZIF-8 MMM consisted of a crack-free and bicontinuous phase with the ZIF-8 nanoparticles uniformly distributed in the PVA polymer. Further evidence was provided by EDX mapping. As shown in Figure S2 e–g, the zinc elemental map indicated a uniform distribution of ZIF-8 on the membrane surface. A cross-sectional SEM image of PVA/ZIF-8 MMM corroborated the homogeneity of the cross-section (i.e., no interfacial voids and no obvious aggregation) throughout the entire membrane (Figure S3 b–d). As the loading of ZIF-8 was increased from 0 to 39 wt %, the thickness of the fabricated membranes also increased from 20 to 50 μm. As membrane thickness affects the pervaporation performance, the permeation flux of the fabricated MMM was determined using membrane permeability which accounts for the membrane thickness. We also confirmed by XRD that crystalline PVA/ZIF-8 MMM (39 wt %) contained both ZIF-8 and PVA (Figure S4).

PVA/ZIF-8 MMMs with different amounts of ZIF-8 were used for the dehydration of an ethanol/water mixture (90:10 w/w) at 25 °C. The separation performance can be determined in terms of the permeation flux (permeability in this study) and the ethanol/water separation factor (for details, see Table S1). As shown in Figure 2 a, both the permeability and the separation factor of the fabricated MMMs increased upon increasing the ZIF-8 nanoparticle loading. For example, in contrast to the permeability and separation factor of pristine PVA membranes (0.75×10^6 Barrer and 543), the values of PVA/ZIF-8 MMM (39 wt %) were significantly larger (2.07×10^6 Barrer and 4725, respectively). The increase in both the permeability and the separation factor suggests a synergistic effect, which we attributed to the following reasons: 1) The increased permeability should be mainly due to the highly porous structure of the loaded ZIF-8 nanoparticles because nanoporous ZIF-8 has a lower resistance to the feed molecules than a pristine PVA matrix. 2) The increased separation factor could be due to molecular sieving effects induced by ZIF-8. Furthermore, the ZIF-8 nanoparticles could inhibit the swelling of the PVA polymer when the PVA/

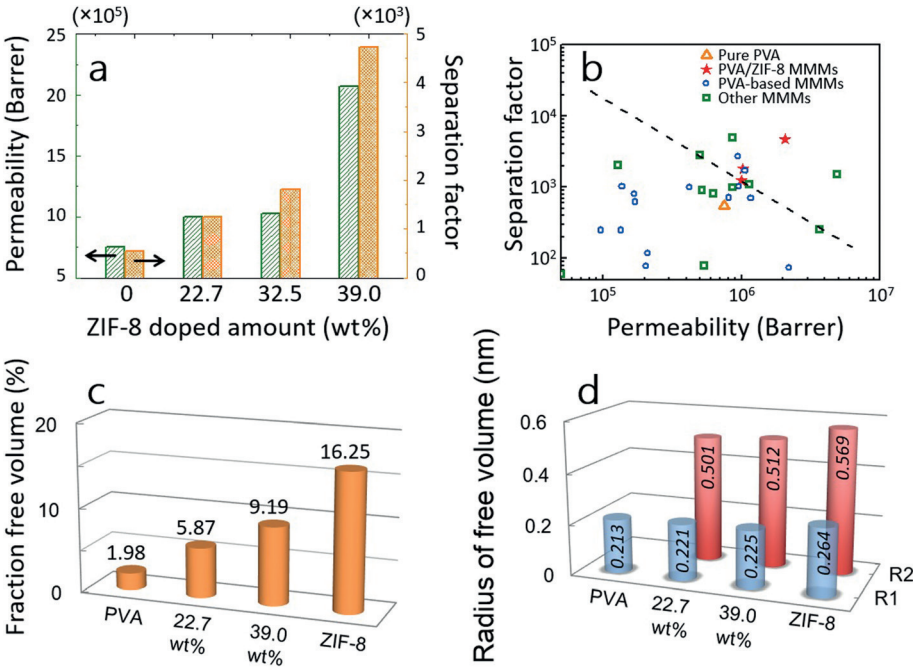

Figure 2. a) H_2O permeability and separation factors of PVA/ZIF-8 MMMs with different ZIF loadings. b) Performance of PVA/ZIF-8 MMMs and membranes from the literature in ethanol dehydration pervaporation. c) Fractional free volumes of PVA, MMMs, and ZIF-8. d) Radii of the free volume of PVA, MMMs, and ZIF-8.

ZIF-8 MMMs are in contact with ethanol/water mixtures. This hypothesis was confirmed by the correlation between the degree of swelling and the weight fraction of ZIF-8 (Figure S5).

The transport properties of organic/inorganic MMMs are highly dependent on the nanostructure of the membranes.[11] According to the separation mechanism in MMMs proposed by the groups of Chung[11] and Kaliaguine,[22] our PVA/ZIF-8 MMMs have an ideal morphology, which can enhance the permeability and the separation factor simultaneously. Once the interfacial voids have formed, the permeant molecules will pass preferentially through the non-selective holes instead of through the nanoporous fillers (i.e., ZIF-8), resulting in poor selectivities.[23] The fillers will also stiffen the polymer chains through strong molecular interactions when the polymer is in close contact with the fillers.[24] Moreover, it is also possible for the polymer chains to penetrate into the nanopores of particles, which leads to pore blockage and no improvement or possibly even a decrease in separation performance.[24] When we compared our PVA/ZIF-8 MMMs with other MMMs from the literature, we found that our MMMs exhibit a better separation performance for ethanol dehydration than others as shown in Figure 2b.

As mentioned above, we attributed the improvement of the separation performance to the high porosity of ZIF-8, and this hypothesis was supported by bulk positron annihilation lifetime spectroscopy (PALS) analysis. The free volume properties of PVA membranes, MMMs, and ZIF-8 nanoparticles in the dry state are summarized in Table S2. According to the literature, a swollen sample can also be analyzed by PALS.[25] Satyanarayana et al. have shown that the probability of positronium formation may be lower in free volume containing water or ethanol than in empty free volume.[25] Figure 2c shows that the fractional free volume (FFV) of a PVA membrane increases from 1.98 to 9.19% upon addition of 39 wt% ZIF-8, which can be attributed to the high porosity of ZIF-8. The increase in the FFV is the reason why the permeability of membrane can be enhanced. On the other hand, the selectivity is more strongly influenced by the free volume in MMMs. The pick-off lifetime (τ_3) of *ortho*-positroniums corresponds to the free volume or cavity size in materials, which means that the longer τ_3 the larger the free volume or cavity. It can be seen that the pure PVA membrane has a τ_3 of only 1.32 ns (Table S2), which can be converted into a pore radius of 0.213 nm using the Tao–Eldrup formula.[26] Upon addition of ZIF-8 in MMMs, we found a significantly longer lifetime of $\tau_{3\text{-}2}$ that corresponds to the cavities in the ZIF-8 nanoparticles. After conversion with the Tao–Eldrup formula, the diameter of the largest sphere that will fit into the ZIF-8 framework is 1.138 nm, which is close to the literature value of 1.160 nm.[14] Figure 2d displays two types of free volume, namely R_1 (smaller pore) and R_2 (larger pore), in MMMs, which correspond to the free volume in PVA and the cavities in ZIF-8, respectively. Apart from R_1 and R_2, we did not observe any other pore structures that are related to the interfacial voids between PVA and ZIF-8, which indicates the homogeneous mixing of PVA and ZIF-8. Consequently, the selectivity can be maintained or even improved. Although the ZIF-8 nanoparticles hinder the packing of PVA chains and induce a slight increase in R_1 (from 0.213 to 0.225 nm), the R_1 value is still small enough to separate water and ethanol molecules. The R_2 values of the MMMs are smaller than in pure ZIF-8, which might be due to the PVA chains partially penetrating into the cages of ZIF-8. Based on PALS analysis, we deduced that the increase in the separation factor is mainly due to the suitable pore aperture of 0.34 nm of ZIF-8 and the reduced swelling (Figure S5) rather than the variation of the free PVA volume (an increase from 0.213 to 0.225 nm).

In conclusion, we have developed a water-based, drying-free process for fabricating a defect-free PVA/nano-ZIF-8 mixed-matrix membrane with a filler loading up to 39 wt%. The PVA/ZIF-8 MMM has an ideal morphology because the water serves as a great medium to bring ZIF-8 and PVA into close contact while the flexible nature of PVA allows it to adapt to and interact with the surface of the ZIF-8 particles. The water-phase and drying-free process effectively solves the

problem of particle aggregation, which is often encountered in conventional MMM syntheses. For dehydrating ethanol, our PVA/ZIF-8 MMM (39 wt%) shows better pervaporation than other PVA-based MMMs. Its permeability is three times larger than that of pristine PVA, and its separation factor is nearly nine times greater. The significant enhancement of the separation performance was attributed to the obvious increase in fractional free volume as determined by positron annihilation lifetime spectroscopy. The PALS data also confirmed that no interfacial voids were formed in between PVA and ZIF-8, indicating that the PVA tightly adhered to ZIF-8. The process presented here could be useful for synthesizing other types of MMM for various membrane applications if it could be adapted to hydrophobic matrix polymers.

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