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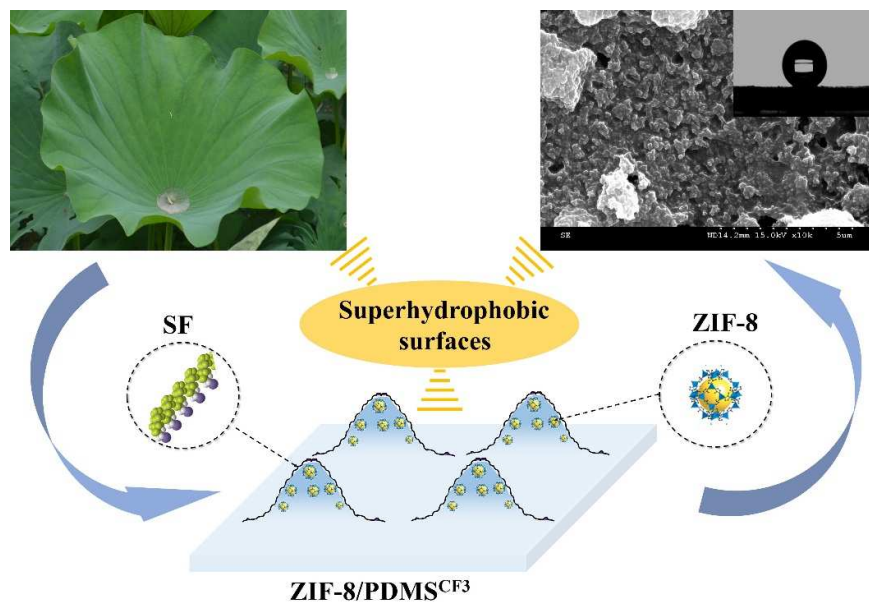


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Inspired by superhydrophobic surface of lotus leaf, ZIF-8/PDMS membrane with micro- and nanoscaled hierarchical structures was modified by SAMs. The as-prepared hierarchical hybrid membrane exhibited excellent performance for bioalcohol pervaporation.

COMMUNICATION

Designing superhydrophobic surfaces with SAMs modification on hierarchical ZIF-8/polymer hybrid membranes for efficient bioalcohol pervaporation

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Inspired by the complementary roles of surface energy and roughness on natural nonwetting surfaces, a superhydrophobic surface has been successfully designed and prepared by self-assembled monolayers modification on hierarchical ZIF-8/polymer hybrid membrane. The as-prepared membrane exhibited the best overall performance for *n*-butanol pervaporation.

Biobutanol is receiving ever more attention as a new liquid fuel.¹ The major challenges in biobutanol production are low butanol titer and product inhibition.^{1b} Therefore, in situ removal of butanol from the fermentation broth by pervaporation may afford a more efficient way of producing biofuel. In recent decades, pervaporation has been widely studied as a useful energy-saving and cost-effective separation technique for liquid mixtures.² Based on the solution-diffusion mechanism for pervaporation, the separation performance of a membrane is mainly affected by its constituent materials and structure. In particular, the membrane surface properties, such as wettability and microstructure, are important factors for pervaporation performance. The more hydrophobic the membrane surface, the more repellent it is to water molecules, and thus more water molecules are excluded. For sorption-diffusion controlled alcohol perm-selective pervaporation, it is crucial to obtain a high sorption selective surface for alcohol molecules. Superhydrophobic surface represents a water contact angle (CA) of > 150° and a slide angle of < 10°.³ However, the reported contact angles of water on alcohol-permselective pervaporation membranes are 90–140°.^{2d} Very few studies have been carried out on superhydrophobic membranes for pervaporation.

The typical natural superhydrophobic surface is that of the lotus leaf, which is attributable to a combination of surface chemistry and roughness on multiple scales (Fig. S2(a), ESI†).⁴⁵ However, this strategy has not been commonly used for designing separation membranes. For pervaporation membranes, the incorporation of

inorganic particles to form a mixed-matrix membrane (MMM) could be an effective way to improve the separation performance. Several types of inorganic materials have been used in making MMMs, such as nano silica,⁵⁶ zeolites,⁶⁷ carbon black,⁷⁸ and MOFs.⁸⁹ In particular, zeolite imidazolate frameworks (ZIFs) can be used to form MMMs with high pervaporation performance due to their hydrophobic inner channels.⁹¹⁰

Unfortunately, for nanohybrid membranes, most studies have been focused on obtaining a uniform distribution of nanoparticles (NPs) inside the MMMs; very few studies have been reported on tuning the surface to superhydrophobic through multiple scales and surface chemistry. In order to further improve the hydrophobicity of nanohybrid membranes, semifluorinated (SF) molecules with CF₃-terminal groups may be deposited on the membrane surface.⁴⁰¹¹ The deposition of self-assembled monolayers (SAMs) formed from organosilanes is a promising technique for applying SF coatings because of the high bonding strength, low surface energy, and high thermal stability of such monolayers.⁴⁴¹² The wettability and free energy of SAMs can be easily controlled by altering the terminal groups from completely hydrophilic (e.g., -OH or -COOH) to very hydrophobic (e.g., -CH₃ or -CF₃).⁴²¹³

In this study, a superhydrophobic surface has been designed by modification with SAMs of a ZIF-8/PDMS nanohybrid membrane. For this purpose, as shown in Fig. 1, a nanohybrid membrane with micro- and nanoscaled hierarchical structures was fabricated, and thereafter its surface was modified with SAMs. Hydrophobic ZIF-8 nanoparticles with flexible structure were incorporated into the PDMS matrix, which affected the surface structure and chain packing of the polymer membrane. After UV/ozone (UVO) treatment and deposition of SF molecules on the ZIF-8/PDMS, the membrane was rendered superhydrophobic because of the formation of an SAM on the hierarchical hybrid surface. The method for fabrication of SAMs is based on combining (i) the creation of -OH groups and (ii) the grafting reaction between SF trichlorosilanes and -OH functionalities present on the silica surface (Scheme S1, ESI†). To create the -OH functionalities, the PDMS was subjected to UVO treatment (UV irradiation at 185 and 254 nm in air).⁴⁴¹⁴ Atomic oxygen and ozone may react vigorously with carbon atoms, forming hydroxyl groups. The adsorbed SF molecules react with the silanol groups present on PDMS^{OH} to yield terminal -CF₃ groups.

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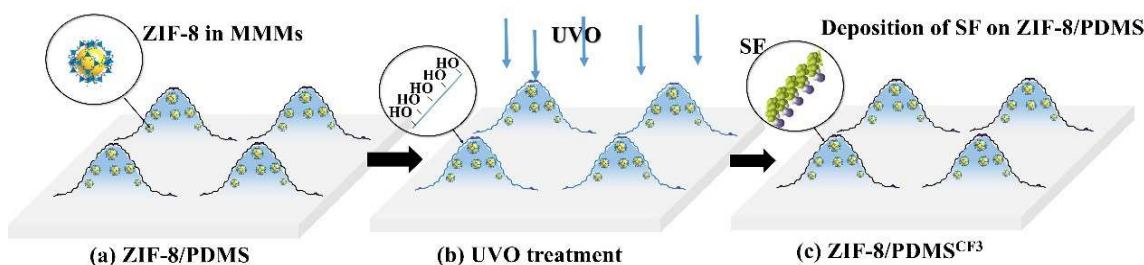


Fig. 1 The schematic diagram describing the preparation of the SAMs-modified ZIF-8/PDMS superhydrophobic membrane.

The morphologies of the ZIF-8 nanoparticles and SAM-modified nanohybrid membranes were examined by SEM. Fig. S2(c) shows the microstructure of the ZIF-8 nanoparticles, which indicated that ZIF-8 NPs with a narrow size distribution (80–90 nm) had been successfully synthesized at room temperature. The ZIF-8 particles exhibited superhydrophobic behavior (water contact angle $>150^\circ$, inset in Fig. S2(a), ESI[†]), which is in good agreement with previous reports.^{9,10(a)}

Subsequently, the as-synthesized nanoparticles were embedded into the PDMS to form a nanohybrid membrane by a dip-coating method. Figs. 2(a), (b), (c), and Fig. S2(d), show the surface microstructures of the PDMS, ZIF-8/PDMS, SAM-modified ZIF-8/PDMS (ZIF-8/PDMS^{CF3}), and SAM-modified PDMS (PDMS^{CF3}), respectively. The surfaces of PDMS and PDMS^{CF3} were smooth and defect-free. Figs. 2 (b), (c), and (d) show that the membranes were very rough, with micro- and nanoscaled hierarchical structures owing to the incorporation of ZIF-8 NPs. During fabrication of the nanohybrid membrane, the NPs may have aggregated after

sonication. This aggregation may have contributed to formation of the hierarchically structured hydrophobic surfaces, which bore some resemblance to the micromorphology of the lotus leaf (Fig. S2(b), ESI[†]). AFM images (Fig. S3, ESI[†]) further confirmed these structures. It was noted that the Ra roughness of the PDMS membrane decreased from 2.43 nm to 2.40 nm after SAM surface modification. The incorporation of ZIF-8 NPs significantly increased the Ra value from 2.43 nm to 57.2 nm. Subsequently, the deposition of SAMs on the UVO-treated ZIF-8/PDMS decreased the Ra value from 57.2 nm to 42.8 nm. Obviously, the film surface became much rougher after ZIF-8 NPs were embedded within it. The enhanced surface roughness could amplify the wettability of membranes.¹⁵ Moreover, the rougher surface of the ZIF-8/PDMS membrane provided more sites for the deposition of SF chains, so that the hydrophobicity could be improved.

To gain a better understanding of the unique morphology of the SAM modification, surface element analysis of the modified PDMS and ZIF-8/PDMS membranes was carried out by EDX (Table S1, ESI[†]). As shown in Table S1, the amounts of Zn and N confirmed that the ZIF-8 NPs had been successfully incorporated into the PDMS membrane. The amount of C decreased after application of the SAM. This indicated that a photo-oxidative reaction involving in situ generated atomic oxygen removed the methyl groups from the polysiloxane precursor (Scheme S1, ESI[†]). Moreover, the increase in the amount of F from 1.87 % to 3.88 % for PDMS^{CF3} and ZIF-8/PDMS^{CF3} indicated that more SF groups were exposed on the hybrid membrane surface. This was because the rougher surface (Fig. S3(d), ESI[†]) of the hybrid membrane resulting from the introduction of NPs provided a much larger reactive area (Fig. 1), which was favorable for the subsequent growth of SAMs. The XRD pattern showed the nanohybrid membrane to be composed of ZIF-8 and to have good crystalline structure (Fig. S4, ESI[†]).^{45,16}

The hydrophobicity of the ZIF-8/PDMS^{CF3} membrane was evaluated by measurement of the water contact angle (inset in Fig. 2). The PDMS membrane without ZIF-8 NPs was modified by SAMs, whereupon the CA of the modified PDMS membrane surface increased from 99° to 108.4° . This result showed that the deposition of SF monolayers led to an increase in the CA, with a maximum of value of less than 120° for smooth CF_3 -terminated surfaces.^{46,17} After the introduction of ZIF-8 nanoparticles, a hydrophobic surface (CA = 145.3°) was formed because of the increase in its roughness (inset in Fig. 2(b)). Although the ZIF-8/PDMS membrane was hydrophobic, a partly uncrosslinked -OH group on its surface was sufficient for the strong adherence of a water droplet, impairing its waterproof ability. This behavior is a serious problem for use of the superhydrophobic surface in alcohol permselective pervaporation. After modification with SAMs, the membrane containing ZIF-8 showed a water CA of 152.3° (inset in Fig. 2(c)). Moreover, the ZIF-8/PDMS^{CF3} membrane showed a small water slide angle of about 5° .

Table 1 Pervaporation performances of different membranes for the separation of 3 wt% *n*-butanol/water mixture

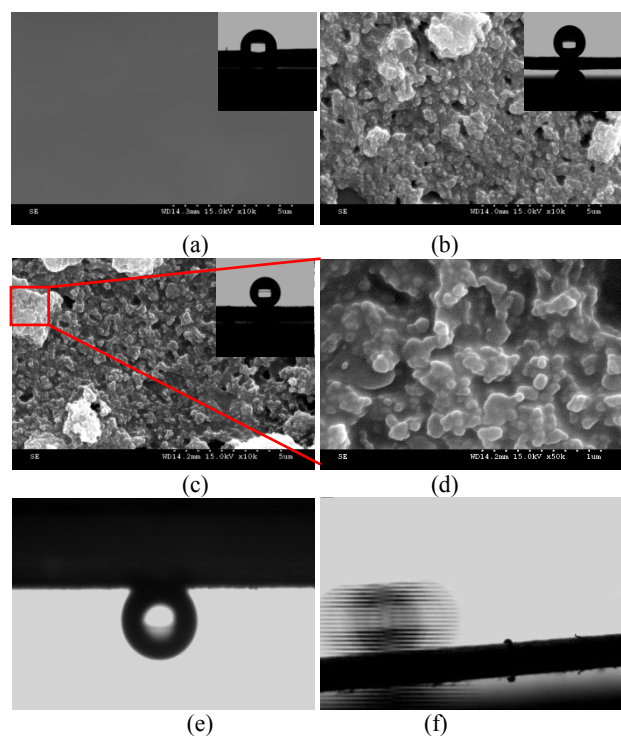


Fig. 2 SEM images of the surface of (a) PDMS membrane, (b) ZIF-8/PDMS membrane, (c) ZIF-8/PDMS^{CF3} membrane, (d) ZIF-8/PDMS^{CF3} membrane; Water sliding angle images of (e) ZIF-8/PDMS membrane, (f) ZIF-8/PDMS^{CF3} membrane; Inset: water contact angle images of (a) PDMS membrane, (CA = 99°); (b) ZIF-8/PDMS membrane, (CA = 145.3°); (c) ZIF-8/PDMS^{CF3} membrane, (CA = 152.4°);

Membrane	Flux (g/m ² ·h)	Separation factor (α)	<i>n</i> -butanol in permeate (wt%)
PDMS	1065	13.4	29.30
PDMS ^{CF3}	1049	19.4	37.52
ZIF-8/PDMS	1459	58.4	64.40
ZIF-8/PDMS ^{CF3}	1339	84.8	72.39

(Experimental conditions: feed of 3 wt% *n*-butanol at 60 °C)

such that water droplets readily rolled off its surface (Fig. 2(f)). It is worth mentioning that in this SAMs method, the SF tended to be deposited over the entire membrane surface and the uncrosslinked -OH disappeared (Fig. 1(c)). Therefore, the interplay of the dual-scale structure and the low surface free energy contributes to this ultra-water-repellent state.

The SAM-modified hybrid membrane was used for the pervaporation separation of *n*-butanol/water mixtures. The separation results are listed in Table 1. It was observed that the separation performance was greatly improved after the incorporation of ZIF-8 NPs and the modification with SAMs. For example, the separation factor increased from 13.4 to 19.7, and the flux decreased from 1065 g/m²·h to 1049 g/m²·h on going from the PDMS to the PDMS^{CF3} membrane. After the incorporation of ZIF-8 NPs, both the separation factor and the flux significantly increased. This was because the ZIF-8 NPs provided butanol-selective channels.^{45,18} The incorporation of ZIF-8 NPs made the membrane surface highly rough and more hydrophobic, thereby repelling most of the water from being taken up on or diffusing through its internal surface. Moreover, after SAM modification, the ZIF-8/PDMS^{CF3} membrane displayed an outstanding separation factor of 84.8 and a flux of 1339 g/m²·h. Additionally, the butanol flux increased from 940 g/m²·h to 969 g/m²·h, and the water flux decreased from 519 g/m²·h to 370 g/m²·h (Table S3, ESI†). This could be attributed to the formation of superhydrophobic separation layers, which could weaken the affinity for water and lead to a much higher separation factor, albeit with slightly decreased flux. Therefore, both the permeation flux and separation factor of the ZIF-8/PDMS^{CF3} membrane were far higher than those of the pure PDMS membrane.

The ZIF-8/PDMS^{CF3} membrane in this work exhibited the best overall separation factor for 1 wt% *n*-butanol/water compared with other membranes reported to date (Table S4, ESI†). The optimal pervaporation performance of the ZIF-8/PDMS^{CF3} membrane with a superhydrophobic surface (CA = 152.4°) afforded an excellent total flux (1041 g/m²·h) and a higher separation factor of 95.8 at a feed temperature of 60 °C.

Conclusions

In conclusion, a simple SAM-modification method has been presented for the fabrication of a superhydrophobic surface on hierarchical ZIF-8/PDMS hybrid membranes. SEM and AFM images have demonstrated that ZIF-8 nanoparticles effectively enhanced the surface roughness of the polymer membrane, which gave rise to a larger reactive area covered by a high proportion of CF₃ groups. This treatment led to formation of a superhydrophobic layer (CA = 152.4°) on the surface of the ZIF-8/PDMS nanohybrid membrane. Moreover, it has been demonstrated that the ZIF-8/PDMS^{CF3} showed both higher selectivity and higher permeability than PDMS for *n*-butanol/water separation. As nanohybrid PDMS membranes play an important role in many processes, such as nanofiltration and gas separation, SAMs-modified MOF/PDMS

membranes may open up significant possibilities for applications in the separation of various mixtures.

Acknowledgements

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