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Short communication

Wettability switchable metal-organic framework membranes for pervaporation of water/ethanol mixtures

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ABSTRACT

To evaluate the effect of MOF surface wettability for the purification of ethanol from water/ethanol mixtures, the hydrophilic Ni_2(L-asp)$_2$bipy membrane is switched to hydrophobic Ni_2(L-asp)$_2$bipy@PDMS membrane via vapor deposition of PDMS. The PDMS coating can improve the hydrothermal stability of MOF membranes. The stable Ni_2(L-asp)$_2$bipy membrane exhibits a high flux of H_2O and acceptable separation factor. The pervaporation studies based on the both two membranes provide insight into the effect of surface wettability on the bio-ethanol purification performance.

To solve the issues of scarcity of fossil resources and environmental pollution, research interests have been focused on the development of renewable and green energy sources, such as bioethanols, in the last decades [1–4]. Bioethanols are mainly obtained through the fermentation of crops to give water/ethanol mixtures, which are then purified to anhydrous ethanol [4–7]. Distillation is one of the conventional processes for the separation of water/ethanol mixture. However, it is challenging to further purify the ethanol when the concentration of ethanol reaches 95.6%, forming an azeotropic solution [8–11]. Additionally, distillation technology is also low-efficiency and non-environmental friendly [9, 12–14]. So, adsorptive separation based on the porous materials has been carried out to remove the remaining water [15–17]. Nevertheless, this method is difficult for continuous operation and cannot be applied to the mixture with low ethanol concentration. Membrane based technology is a promising approach for the water/ethanol separation, because of its considered eco-friendness with operational ease and high efficiency [18]. Pervaporation and membrane distillation processes are attractive in the membrane separation for the ethanol purification, which require hydrophilic or hydrophobic property of membrane materials [19]. The separation performance of the pervaporation process is mainly determined by the composition, structure and property of the membrane [20–22].

Many membrane materials have been studied for the pervaporation separation of water/ethanol mixture, including porous inorganic membrane and polymer membrane [23]. For the polymer membrane, there is a famous hydrophobic polymer material poly(dimethyl siloxane) (PDMS), which is referred to as "silicone rubber" and usually used to fabricate hollow fiber, tubular, unsupported sheet, or thin layer supported sheet membranes [23]. Other species can be doped into the PDMS membrane, forming mixed matrix membranes (MMMs) to enhance the separation performance [24–27]. For the porous inorganic membrane, zeolite membrane, such as NaA, possesses both higher water/ethanol separation factors and fluxes than polymer membranes due to the advantages of uniform pore size (4.2 Å), high surface area, and strong adsorption capacity [28–30].

As an emerging class of porous material, metal-organic frameworks (MOFs) have attracted wide interests in the fields of sensor, catalysis, adsorption and separation owing to their multi-functionality and designability [31–35]. In the previous work, a hydrothermal stable MOF structure of Ni_2(L-asp)$_2$bipy has been made into membranes and their separation performances have been investigated on the gas mixture and racemic isomers [36,37]. To further utilize its uniform pore size (3.8×4.7 Å) and stability, in this study, Ni_2(L-asp)$_2$bipy membrane was prepared on porous SiO_2 disc for separation of water/ethanol mixture in pervaporation process. In the following step, the wettability of Ni_2(L-asp)$_2$bipy membrane was switched to hydrophobicity by the PDMS coating and was also evaluated for the separation of ethanol from water via pervaporation [38]. The pervaporation studies using Ni_2(L-asp)$_2$bipy and Ni_2(L-asp)$_2$bipy@PDMS membranes provide insight into the effect of surface wettability switching on the performance of bio-ethanol purification.

The polycrystalline Ni_2(L-asp)$_2$bipy membranes were fabricated on porous SiO_2 discs by a seeding-secondary growth method (Fig. 1). The

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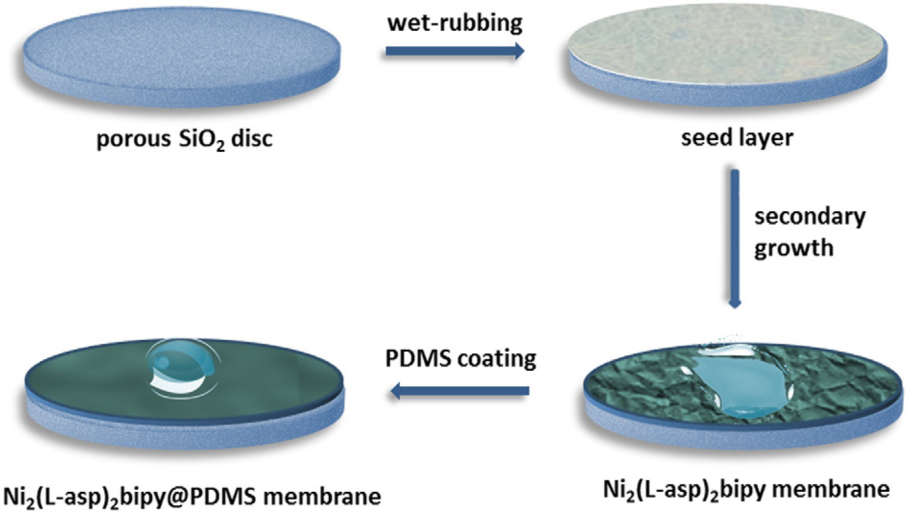

Fig. 1. Schematic illustration of the preparation process of Ni$_2$(L-asp)$_2$bipy and Ni$_2$(L-asp)$_2$bipy@PDMS membranes and water/ethanol separation on them.

seed layer was formed by coating the seed powder grinded from the crystals on the top surface of SiO$_2$ discs by a wet-rubbing method. The seed powder was evenly riveted in the gaps between particles of the porous SiO$_2$ discs during the rubbing and solvent evaporation process. After a solvothermal reaction, continuously grown Ni$_2$(L-asp)$_2$bipy membrane was successfully prepared. Then, a vapor deposition of PDMS was applied to the as-synthesized Ni$_2$(L-asp)$_2$bipy membrane to switch the hydrophilic surface into hydrophobic. Powder X-ray diffraction was carried out on to confirm the structure of the obtained membranes. As the results shown in the Fig. 2, no peaks of other phases are detected, indicating that the Ni$_2$(L-asp)$_2$bipy membrane is of a pure phase, which is maintained well after deposition of PDMS.

The SEM images of the membranes are shown in Fig. 3, which suggest that defect free Ni$_2$(L-asp)$_2$bipy membranes were prepared by the seeding-secondary growth method. From the images of Fig. 3a, b, d and e, no noticeable differences in membrane morphology are found between the as-prepared Ni$_2$(L-asp)$_2$bipy membrane and the Ni$_2$(L-asp)$_2$bipy @PDMS membrane, which is consistent with the PXRD results. More morphology information of the membranes can be found in the supporting information, including the top view and cross-section SEM images of the support (Fig. S1), seed layer, Ni$_2$(L-asp)$_2$bipy and Ni$_2$(L-asp)$_2$bipy @PDMS membranes.

The hydrophobicity of the modified membrane was evaluated by the measurement of the water contact angle (CA). The Ni$_2$(L-asp)$_2$bipy membrane is hydrophilic and the membrane is wetted as soon as the water drop falls on its surface (Fig. 3c), giving a water contact angle close to 0°. The membrane after PDMS modification exhibits a water CA of 137.1° (inset of Fig. 3e), suggesting the successful switching of the wettability of membrane surface from hydrophilicity to hydrophobicity. This conversion is also confirmed by the optical images of the membrane before and after PDMS deposition, as shown in Fig. 3c, f. FTIR spectra (Fig. S2) were carried out to confirm the PDMS coating on the membrane surface. The band showed up at 1260 cm^{-1} can be assigned to the interaction between the Si(CH$_3$)$_2$ groups and the Ni$_2$(L-asp)$_2$bipy framework [39]. The Ni$_2$(L-asp)$_2$bipy@PDMS membrane was also studied by TGA (Fig. S3) and the results confirmed that there is no obvious weight loss below 300 °C, which proves the high stability of PDMS coating on the MOF membrane. Since the hydrothermal stability of MOF membranes is one of the key problems for pervaporation applications [40], both Ni$_2$(L-asp)$_2$bipy and Ni$_2$(L-asp)$_2$bipy@PDMS membranes were immersed in the DI water at 80 °C for 24 h. As the PXRD and SEM results shown in Fig. S4, most of the crystals in Ni$_2$(L-asp)$_2$bipy membrane was destroyed, while the structure and morphology of Ni$_2$(L-asp)$_2$bipy@PDMS membrane were maintained after hydrothermal treatment, only causing a slightly intensity loss of PXRD peaks, which suggests that the PDMS coating can improve the hydrothermal stability of MOF membranes.

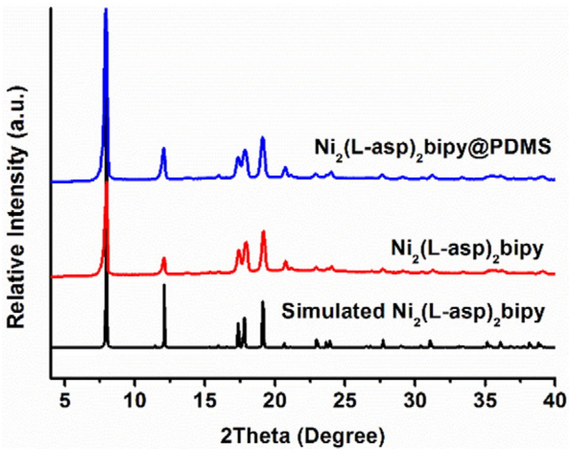

Fig. 2. Powder X-ray Diffraction (PXRD) patterns of the simulated Ni$_2$(L-asp)$_2$bipy, Ni$_2$(L-asp)$_2$bipy membrane and Ni$_2$(L-asp)$_2$bipy@PDMS membrane.

Ni$_2$(L-asp)$_2$bipy shows not only a high stability but also a permanent porosity with uniform pore size (3.8 × 4.7 Å) and high BET surface area (247 m^2 g^{-1}) [41]. This narrow pore size distribution is suitable for the separation of H$_2$O (2.8 Å) and ethanol (4.7–5.1 Å) molecules. The porosity properties of Ni$_2$(L-asp)$_2$bipy and Ni$_2$(L-asp)$_2$bipy @PDMS membranes were characterized by the physical gas adsorption (Fig. S5). The powder sample scraped from the Ni$_2$(L-asp)$_2$bipy membrane possesses a BET surface area of 178 m^2 g^{-1}. The slight reduction in surface area compared with Ni$_2$(L-asp)$_2$bipy crystal is caused by mixing with the SiO$_2$ scraps from the substrate. As shown in Fig.S5, the CO$_2$ adsorption curve of Ni$_2$(L-asp)$_2$bipy@PDMS membrane at 195 K is similar with the Ni$_2$(L-asp)$_2$bipy membrane, indicating the maintained porosity after PDMS deposition. The calculated BET surface area of Ni$_2$(L-asp)$_2$bipy@PDMS membrane is about 159 m^2 g^{-1}, which is only a bit lower compared with original membrane.

Encouraged by the suitable porous environment of Ni$_2$(L-asp)$_2$bipy structure, the pervaporation performances of Ni$_2$(L-asp)$_2$bipy membrane vs. Ni$_2$(L-asp)$_2$bipy@PDMS membrane were investigated for the separation of water from water/ethanol mixtures. The fluxes and separation factors (α_i) are summarized in Fig. 4, Table S1 and S2 with varied ethanol concentration in the feed solution. For the Ni$_2$(L-asp)$_2$bipy membranes, as shown in the Fig. 4a and b, water is the preferred permeating component compared with ethanol, giving a concentrated ethanol

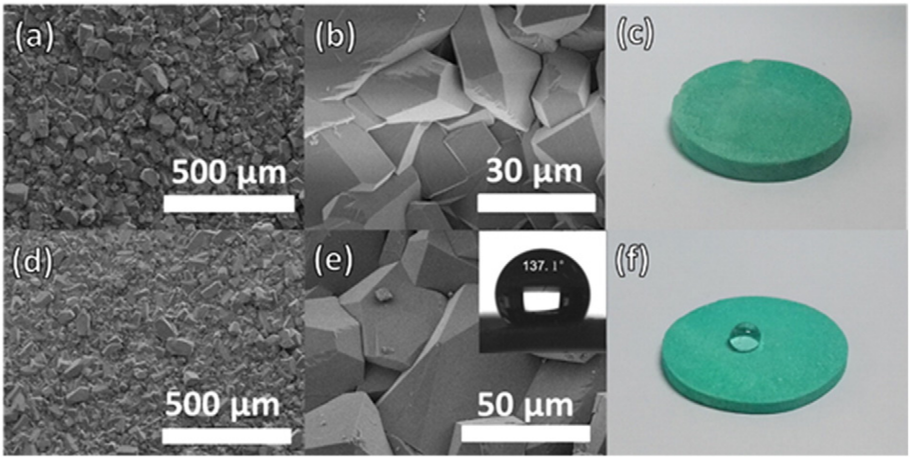

Fig. 3. (a, b) Top view SEM images of different magnification of Ni_2(L-asp)$_2$bipy membrane; (d, e) top view SEM images of different magnification of Ni_2(L-asp)$_2$bipy@PDMS membrane. Inset: water contact-angle of Ni_2(L-asp)$_2$bipy@PDMS membrane; (c, f) optical photos of the Ni_2(L-asp)$_2$bipy membrane and Ni_2(L-asp)$_2$bipy @PDMS membrane.

in retentate, which is due to the molecular sieving and hydrophilic property of the MOF membrane. As the concentration of ethanol in the feed solution increased from 50 to 90 wt%, the α_i varies from 73.6 to 12.8, and the water flux decreases from 27.6 to 2.66 $kg \cdot m^{-2} h^{-1}$, while the flux of ethanol is moderately changed. The reason leads to this phenomenon is that the increased ethanol molecules in the feed side block the channels of the membrane, hindering the diffusion of water. As the temperature rising from 30 °C to 60 °C, the flux of water increased from 27.6 to 36.3 $kg \cdot m^{-2} h^{-1}$ under 50 wt% ethanol concentration, which is due to the larger kinetic energy of liquid molecules. And a low separation factor of 60.1 was obtained at 60 °C.

To evaluate the effect of MOF surface wettability on the purification of ethanol from water/ethanol mixtures, the PDMS deposited membranes were also applied to the pervaporation process. For the Ni_2(L-asp)$_2$bipy@PDMS membrane, lower water fluxes are obtained due to the weak affinity between the hydrophobic membrane surface and water. The reduced water fluxes and increased ethanol fluxes lead to decreased separation factors, as illustrated in Fig. 4c and d. Similar with the trend of Ni_2(L-asp)$_2$bipy membrane, lower separation factor is obtained as the ethanol concentration enhanced. When the ethanol concentration reaches 90% at 60 °C, α_i of water/ethanol is even lower than 1, which means that ethanol has become the selective permeating component of the Ni_2(L-asp)$_2$bipy@PDMS membrane. Although this result indicates that the Ni_2(L-asp)$_2$bipy@PDMS membrane maybe not suitable for ethanol purification, the hydrophobic surface suggests that it is a promising candidate membrane for membrane distillation.

In summary, continuously grown Ni_2(L-asp)$_2$bipy membrane was prepared on the porous SiO_2 discs by a seeding-secondary growth method. Vapor deposition of PDMS was carried out to switch the hydrophilic surface of the membrane into hydrophobic. The porosity of membrane was maintained after PDMS coating, and the hydrothermal stability of MOF membranes were enhanced. Pervaporation water/

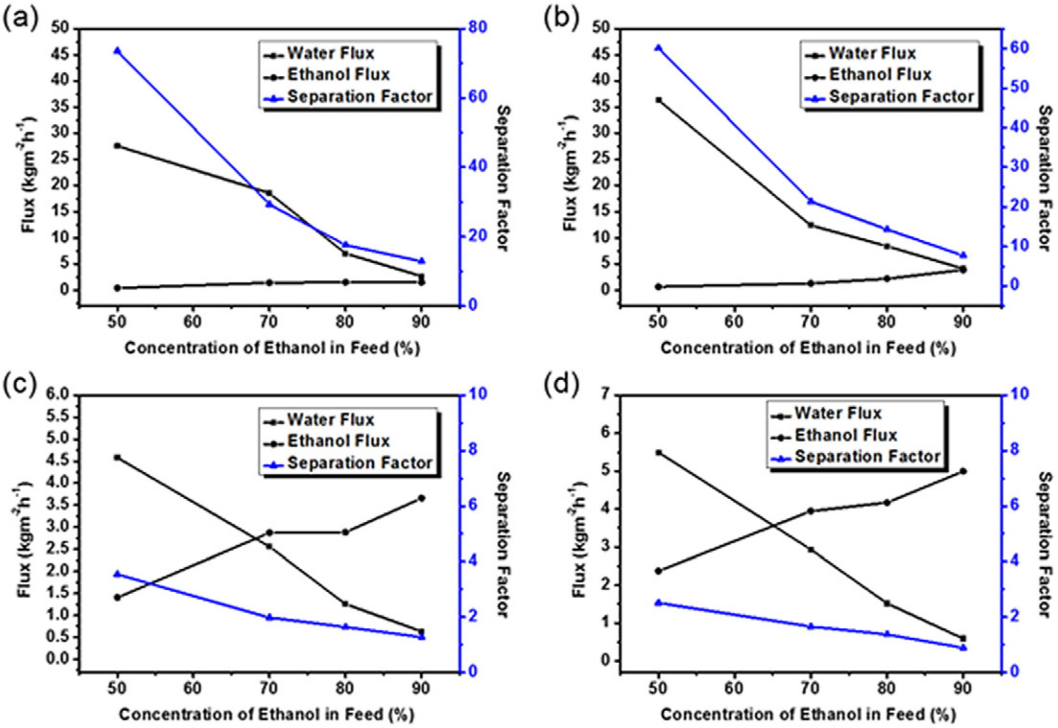

Fig. 4. Effect of ethanol concentration in feed solution on the separation factor and flux at (a) 30 °C and (b) 60 °C for Ni_2(L-asp)$_2$bipy membrane. Effect of ethanol concentration (wt%) in feed solution on the separation factor and flux at (c) 30 °C and (d) 60 °C for Ni_2(L-asp)$_2$bipy@PDMS membrane.

ethanol separation process was evaluated on both of the two stable membranes. At the temperature of 30 °C, Ni_2(L-asp)$_2$bipy membrane possesses a remarkable high flux of 27.6 kg·m^{-2} h^{-1} and a separation factor of 73.6 for water/ethanol mixture with 50 wt% ethanol. The developed Ni_2(L-asp)$_2$bipy@PDMS membrane exhibits a lower separation factor due to its hydrophobic surface, which may be applied to the membrane distillation for water/ethanol separation. The pervaporation studies using these two membranes provide insight into the effect of surface wettability on the bio-ethanol purification performance.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2017.05.016.

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