Organic-inorganic nanocomposite membranes for molecular separation and bioapplications

J Hou¹,², P D Sutrisna³, L Li⁴ and V Chen¹

¹School of Chemical Engineering, University of Queensland
²Department of Materials Science and Metallurgy, University of Cambridge
³School of Chemical Engineering, University of Surabaya, Indonesia
⁴School of Chemical Engineering, University of New South Wales, Australia

E-mail: Jingwei.hou@uq.edu.au

Abstract. Novel porous materials like metal organic frameworks have shown good promise in catalysis, separation, sensing and adsorption. Compared with the conventional polymeric membranes, metal organic framework membranes usually exhibit higher separation efficiency. However, there are still many challenges which need to be addressed, like the interfacial compatibility within the mixed matrix membrane, defective engineering and stability of the framework stability. We will discuss our strategies to solve these problems towards better membranes. On top of the conventional separation membranes, metal organic framework materials can be applied to construct the artificial cellular membranes for bioentities and even living cells. The porous crystal provides exoskeleton to protect the soft biomolecules and their combination can enable a series bioapplications like catalysis, drug delivery and drug release.

1. Introduction
Metal organic framework materials have been recognized as one of the most promising candidates for separation and energy applications. It has a large surface area, controllable porous structure and chemical properties, and surface functionalization capability. Currently, the total structure of metal organic framework materials has reached over 60,000 of different types. However, its application, especially as a separation device, is still limited due to its difficulty in assembly into practical devices without introducing extra defects, which is extremely important for the membrane separation process as the presence of any defects can impose significant negative effect on the separation efficiency. The selectivity can be compromised by the microdefects on the membrane. In this contribution, we would like to introduce some of our recent contribution in this line of research, by regulating the interfacial compatibility between metal organic frameworks and polymeric, continuous supports, to fabricate better membrane devices toward their potential application in water treatment, gas separation, and energy-related applications [1, 2].

2. Compositing zeolite imidazolate framework-8 with polymeric supports
Zeolite imidazolate framework is usually constructed by the Zn, Co metal ions, interconnected by imidazolate ligands. The framework structure is very similar to that of the inorganic silica-based porous zeolite material. The pore size of the zeolite imidazolate framework can be regulated at the size range of gas molecules, e.g. CO₂ and N₂, thus it has been regarded as a promising candidate for molecular separation for gaseous mixtures. One of the early attempts from us, is to blend one type of zeolite imidazolate framework (ZIF-8) with the polymeric support (Figure 1) [3, 4], and the resultant
membranes were tested for CO\(_2\) and N\(_2\) separation. Though the loss of selectivity was observed after the incorporation of ZIF-8 (i.e. the membrane has the lower capability to separate CO\(_2\) from N\(_2\)), the membrane exhibited a significantly improved permanence (gas flow rate). In addition, one of the common problems for the polymeric membrane is its instability under the industrial-related operational conditions, like high temperature and elevated pressure. The inherent flexible, porous polymeric chain can experience compaction and rigidification, leading to the loss of separation efficiency. What we discovered through our research is that due to the satisfactory interfacial compatibility between ZIF-8 nanocrystals and their surrounding polymeric matrix, the formed hydrogen and pi-pi interaction can help stabilize the polymeric membrane structure, even at challenging operational conditions.

**Figure 1.** Schematic diagram of the ZIF-8/polymer mixed matrix membrane, and the mechanism of their improved operational stability under an elevated pressure condition.

Since the presence of high porosity of the ZIF-8 nano-crystals, it is ideal to assemble the nano-crystal to form a coherent, continuous film to realize efficient separation. However, the as-synthesized ZIF-8 materials are usually in the form of discrete powder form, and it is difficult to assemble it into practical devices: the process ability of the nano-crystal is low, as it does not dissolve in solvents without compromising its porous structure. Recent advance in metal organic framework hot pressing can be inapplicable for membrane fabrication as well due to the difficulty to form a thin layer for separation. Ideally, a coherent film can be formed via *in-situ* heterogeneous crystallization and crystal growth of ZIF-8 of top of polymeric support. However, due to the limited compatibility between the crystal phase and polymeric phase, the heterogeneous nucleation efficiency can be limited, restricting the formation of a high-quality film. We proposed a concept to solve this problem, by introducing an interfacial mediate layer, composed of TiO\(_2\) nanoparticles, to promote the growth and formation of ZIF-8 on a polymeric support. The polymeric porous support was firstly coated with a layer of nano-sized TiO\(_2\) nanoparticles, followed by surface functionalization of amine groups to promote the heterogeneous nucleation of ZIF-8. The fabricated composite membrane has a thickness of 400 nm for the ZIF-8 layer, with its good alignment of the crystal structure with the pristine ZIF-8 powder (as suggested by the powder XRD results). Then the coherent, macroscope defect-free ZIF-8 layer showed satisfactory molecular sieving behaviour, exhibiting highly efficient H\(_2\) and CO\(_2\) separation efficiency. The practical membrane performance has good agreement with the theoretical estimations of the pure ZIF-8 layer, suggesting the separation is achieved via the ZIF-8 layer [5].
Figure 2. Formation of the coherent ZIF-8 coating layer on polymeric membrane surface. (a) Structure of the composite membrane, composed of polymeric PVDF support, surface coated TiO$_2$ layer and ZIF-8 top coating layer. (b-c) Surface and cross-sectional SEM image for the ZIF-8 membranes. (d) Elemental mapping results of the composite membranes, showing the presence of Zn elements on the ZIF-8 layer. (e-f) Crystal structure analysis and gas adsorption profiles of the membranes subject to different treatment [5].

3. Interfacial engineering to improve the membrane performance
As stated above, the presence of micro defects for membrane can lead to the loss of separation efficiency. However, the defect engineering for metal organic frameworks has been attracting increasing attention as it can induce extra functions for the materials. For example, the loss of metal ion or organic ligands can generate under-coordinated metal clusters, which further promote the catalytic efficiency and adsorptive capacity. In order to incorporate the defective yet functional metal organic framework materials into the membrane, we specifically engineered a type of topologically engineered metal organic framework material, with the presence of surface mesoporous structures, on top of the inherent microporous framework (Figure 3). The resultant materials exhibited a significantly improved water uptake from brine, showing good potential as pervaporation desalination membranes. After subsequent blending of the engineered crystal into substrates, we managed to fabricate a series of composite membranes, showing an improved brine desalination performance: compared with benchmark counterparts, the composite pervaporation membrane exhibits a nearly 100 % improvement in terms of the water productivity, and it maintained nearly 100 % rejection of the salts. This membrane technology has been considered one of the most promising candidates for challenging brine (e.g. 300 g/L NaCl solution) treatment (Figure 4).
4. Bioapplications
Recently, we have demonstrated that the MOF materials can composite with biomolecules, providing an extra protective layer for bioentities against challenging environments. However, their practical application is still hampered by the limited chemical stability of MOF, due to the relatively weak coordinative bond between the metal ions and organic ligands. We have developed a bonding hybrid approach, to incorporate a carboxylate group into the pristine MOF structure, and the composite materials exhibit a significant improved stability against various challenging environments.

5. Conclusion
The development of material science provides numerous opportunities enabling the development of nanocomposite materials to realize advanced functions. This contribution summarizes the recent progress in this line of research in our group, through which we hope to shed light on the future development of a metal organic framework based nanocomposite membranes, and the development of the crystal materials at the same time.
References

[1] Ameloot R, Vermoortele F, Vanhove W, Roeffaers M B J, Sels B F and De Vos D E 2011 Interfacial synthesis of hollow metal–organic framework capsules demonstrating selective permeability Nat. Chem. 3 382–7

[2] Banerjee R, Phan A, Wang B, Knobler C, Furukawa H, O’Keefe M and Yaghi M 2008 High-Throughput Synthesis of Zeolitic Imidazolate Frameworks and Application to CO₂ Capture. Sci. 319 939–43

[3] Sutrisna P D, Hou J, Li H, Zhang Y and Chen V 2017 Improved operational stability of Pebax-based gas separation membranes with ZIF-8: A comparative study of flat sheet and composite hollow fibre membranes J. Membr. Sci. 524 266–79

[4] Sutrisna P D, Hou J, Zulkifli M Y, Li H, Zhang Y, Liang W, D’Alessandro D M and Chen V 2018 Surface functionalized UiO-66/ Pebax-based ultrathin composite hollow fiber gas separation membranes J. Mater. Chem. A 6 918–31

[5] Hou J, Sutrisna P D, Zhang Y and Chen V 2016 Formation of Ultrathin, Continuous Metal–Organic Framework Membranes on Flexible Polymer Substrates Angew. Chem. Int. Ed. 55 3947–51

[6] Liang W, Li L, Hou J, Shepherd N D, Bennett T D, D’Alessandro D M and Chen V 2018 Linking defects, hierarchical porosity generation and desalination performance in metal–organic frameworks Chem. Sci. 9 3508–16

[7] Gao S, Hou J, Deng Z, Wang T, Beyer S, Buzanich A G, Richardson J J, Rawal A, Seidel R, Zulkifli M Y, Li W, Dennett T D, Cheetham A K, Liang K and Chen V 2019 improving the Acidic Stability of Zeolitic Imidazolate Frameworks by Biofunctional Molecules Chem 5 1597-1608