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Metal-organic frameworks (MOFs), which are emerging porous materials composed of metal ions/clusters and organic linkers, exhibit great advantages in membrane separations due to their well-defined and tunable pore structure. In particular, MOF-based composite membranes that combine the excellent separation capability of MOFs with the processability of polymers are promising for liquid separations. However, the separation performance of the present MOF-based composite membranes is usually limited by poor interfacial bonding between MOFs and polymers. Among many appealing characteristics of MOFs, their tailorable nature enables MOFs to impart desirable properties by surface modification, such as stability, hydrophilicity/hydrophobicity, and dispersibility. In this thesis, I aimed to overcome the limitations of MOF-based composite membranes for improving liquid separation performance by chemically engineering MOF surfaces (Fig. 1). Here, zeolitic imidazolate framework-8 (ZIF-8), one of the most stable MOFs, was employed as a scaffold and the main research results are as follows:

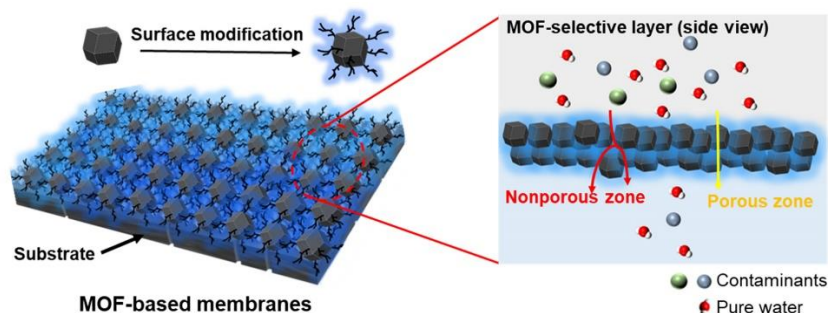


Fig. 1. Schematic illustration of MOF-based composite membranes for liquid separation.

Surfactant-stabilized oil-water emulsions (including oil-in-water and water-in-oil emulsions) are especially difficult contaminants to separate. In **Chapter 2**, membranes prepared by sequential deposition of ZIF-8 microparticles followed by nanoparticles on a regenerated cellulose substrate were applied for oil-water emulsion separation. In order to separate both oil-in-water and water-in-oil emulsions, hydrophobic modification of ZIF-8 was performed via ligand exchange reaction to switch the surface properties of the original particles from hydrophilic to hydrophobic. The unmodified-membranes were effective in separating oil-in-water emulsions due to their relative hydrophilicity, while the hydrophobic modification of ZIF-8 enabled membranes to separate water-in-oil emulsions successfully.

To separate species of a smaller size, in **Chapter 3**, I focused on ZIF-8-based thin-film nanocomposite (TFN) membranes for desalination, where surface modification was performed on ZIF-8 nanoparticles by polydopamine (PDA) coating, and the modified ZIF-8 nanoparticles were incorporated into polyamide as a selective layer supported by a polyethersulfone membrane. The PDA coating improved the dispersibility, chemical stability, and hydrophilicity of ZIF-8 nanoparticles, leading to good separation performances (permeability: $11.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$; Na_2SO_4 rejection: 95.1% with 20 wt% of PDA-coated ZIF-8 in the selective layer) for the membranes.

In general, increasing the MOF loading in MOF-based TFN membranes tends to increase permeability due to additional transport channels. However, this is accompanied by a deterioration in the selectivity because of MOF agglomeration and interfacial failure, which restricts the effectiveness of MOF loading. In **Chapter 4**, I proposed a breakthrough method to fabricate a ZIF-8-matrix nanocomposite membrane with ultrahigh ZIF-8 loading (70 wt%) by using polyethyleneimine-grafted ZIF-8 nanoparticles with film-forming ability as building blocks. Such design exhibited ultrahigh permeability ($43.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) while maintaining comparable selectivity (95%).

In conclusion, the surface engineering of MOF nanoparticles has provided a smart strategy to maximize the advantages of MOFs' nanochannels and alleviate their interfacial failure in designing MOF-based membranes for liquid separation.

Keywords: Membranes; metal-organic frameworks; liquid separation; interfacial bonding; surface modification.