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## MOFs Modified Membranes for Liquid Separation

To cite this article: Wentao Xu *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **493** 012066

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# MOFs Modified Membranes for Liquid Separation

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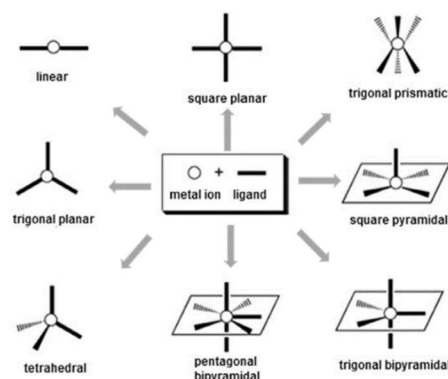
**Abstract.** MOFs are a new sort of crystalline materials made from metal units and organic linkers with greatly designable pore structure and specific surface area. Due to unique crystalline porous materials, high surface area and better compatibility, MOFs has been investigated in the many fields of gas separation, drug release and water separation. The MOF/polymer hybrid membranes have also been attractive in the improved permeability and well-maintained solute rejection benefited from the excellent ability of MOFs, especially higher water flux, better antifouling performance and higher protein retention. In general, the MOF/polymer hybrid membranes with unique performances have attracted the most promising attention for addition of membranes.

## 1. Introduction

Many technologies of separation are being developed to supply potable water to humans, for example, condensation and distillation, which are always regarded as energy-intensive processes in most of industries. Compared with the above techniques, membrane separation exhibits the following advantages such as solution desalination and purification owing to the high separation efficiency, low cost, easy operation and environmentally friendly [1,2,3]. All these advantages will contribute to the wide use of the membrane technology in vast treatment fields.

Among the membranes of water treatment, ultrafiltration membrane has played an important role due to its appropriate porosity. Many suitable materials have been selected to prepare ultrafiltration membrane such as PS, PES, PVDF, PVC and etc. A crucial problem of the ultrafiltration membrane is membrane fouling which impacts the application of wastewater treatment. The membrane fouling usually causes a severe decrease in permeation flux which results in the requirement for more energy, chemical cleaning, material replacement and expensive maintenance costs [4]. Since the charges, roughness, wettability and functional groups of surfaces will change the properties of membranes, many works have been done to investigate interaction of surface modification and fouling [5-6]. Recent progresses showed that hydrophilic surface of membranes had less tendency to fouling. The hydrophilic polymers, zwitterionic species, nanoparticles and carbon materials have been demonstrated as effective and stable modifiers for improving hydrophilicity. [7]

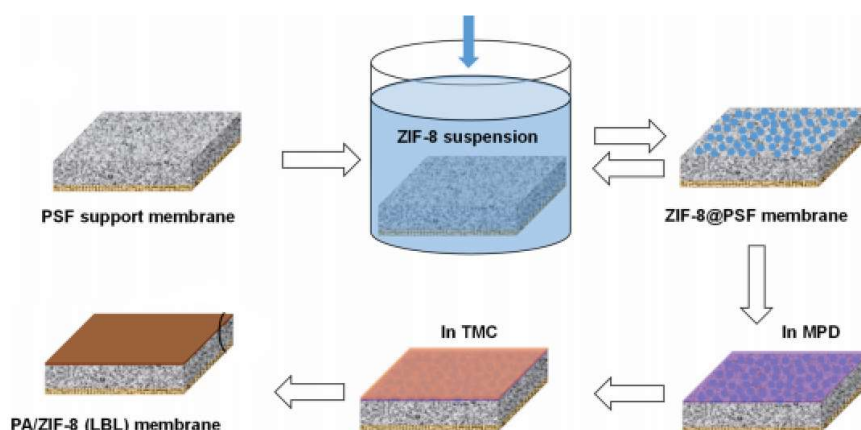




**Figure 1.** Coordination geometries of transition metal ions.

Nanoparticles such as silica nanoparticles [8],  $\text{TiO}_2$  NPs [9] and tunicate cellulose nanocrystals [10] have been investigated as addition of hybrid materials, and related good performance on separation and antifouling have been obtained. However, one issue is that the inorganic nanoparticles like  $\text{TiO}_2$  nanoparticles without modification are hard to make dispersion uniformly in polymeric matrix due to the aggregation and more likely tends to be dropped from the matrix during application. It is necessary to modify the membranes with inorganic materials before use. Another issue is the possible release of nanoparticles from the hybrid membrane, which will raise safety and health concerns[11]. To solve the above problems of membrane modified by nanoparticles, nanoparticles were modified to prepare an attractive alternative which were used as additive of membranes, such as  $\text{SiO}_2$ @N-alamine,  $\text{SiO}_2$  anchored by carboxyl group, MWCNTs modified by surface coating,  $\text{TiO}_2$  grafted by (P(HEMA)), and so on[12].

As new organic-inorganic materials [13], metal-organic frameworks (MOFs) are sort of materials with attractive virtues like ultra-low densities, discrete ordered structure, thermal stability, large surface area beyond  $6000 \text{ m}^2/\text{g}$ , ease of fabrication and broad-spectrum of characteristics suited for chemical and physical applications. The base synthesis of MOFs is shown in Figure 1[14-16]. MOFs with high surface area and rich porosity have been applied in gas capture, membrane separation, chemical sensing and drug delivery, catalyst successfully [17,18]. Recently, MOF membranes based on fascinating MOFs materials have shown excellent separation performances [19].

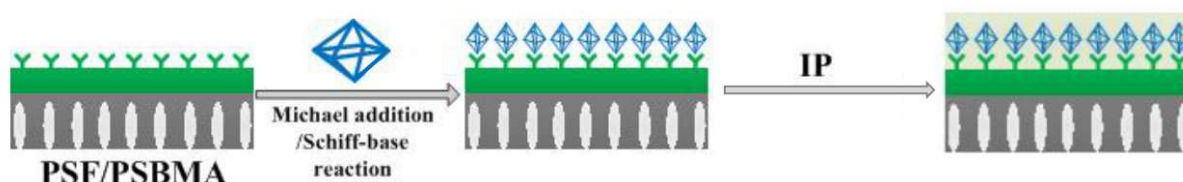


**Figure 2.** Schematic of in situ preparation of nanocomposite membrane.

## 2. The Preparation of MOFs Modified Membranes

One of the main methods for fabrication of MOFs modified membranes is phase inversion which is induced by the technique of immersion precipitation and in situ thin film manufacture. For example, RO and nanocomposite membranes were always prepared by in situ growth method. Campbell et al. produced hybrid MOF membranes by in-situ growth (ISG) of HKUST-1 within the nanopores of polyimide membranes[20]. As shown in Figure 2, Wang et al. reported a new layer-by-layer (LBL) synthesis to fabricate a multilayer structured PA/ZIF-8 nanocomposite membrane[21]. Zirehpour et al. used phase inversion method to prepare asymmetric FO mixed matrix membranes for the application of forward osmosis (FO) desalination [22].

Phase inversion induced by immersion precipitation technique is common method to fabricate hybrid ultrafiltration membranes. As shown in Figure 3, Sun et al. successfully prepared UiO-66-PSBMA modified UF membranes with enhanced hydrophilicity by the method of a phase-inversion method. The prepared membrane exhibited improved water flux and excellent antifouling behavior without sacrificing any protein retention[23].



**Figure 3.** Schematic of the preparation of UiO-66-PSBMA modified UF membranes by phase-inversion method

## 3. MOFs Modified Membranes Used for Liquid Separation

### 3.1. Ultrafiltration membranes

Ultrafiltration membranes have been widely used for water treatment. For industrial ultrafiltration processes, good solute rejection, high flux and high antifouling performance are usually needed, which mainly depend on the surface property and pore structure of UF membranes [4,5]. Generally, the ultrafiltration membrane always faces the fouling phenomenon, and one of the effective ways to solve such issues is to increase the surface hydrophilicity in membrane. However, membrane matrixes are always an inherent hydrophobicity, meaning that hydrophilic modification is necessary.

The advantages of MOFs materials can make MOF/polymer hybrid membranes with improved permeability as well as good solute rejection. Consequently, they are being Compared with the traditional inorganic materials, MOFs hold better compatibility with the soft polymer matrices and own high surface area and controlled porosity. According to the properties of MOFs, MOFs modified ultrafiltration membranes were prepared by researchers. Gholami et al. prepared TMU-5 modified ultrafiltration membranes which possessed big advantages in oil-water separation[24]. Sotto et al. prepared Zn/Co-MOF-74 modified ultrafiltration membranes which had good structural strength in polymer matrix and maintained stability in different BSA solution[25].

Although MOFs possess rich organic ligands, they are actually crystals and exhibit the characteristics of inorganic crystal. It is often difficult to obtain homogeneous MOF dispersion and correspondingly a uniform film through simply direct dispersion of MOF particles in polymeric solution. The functionalization of MOFs is a way to solve the problem[17], and therefore successfully used to improve the hydrophilicity and the dispersion of ultrafiltration membranes. Sun et al. studied UiO-66-PSBMA/PSf membrane and found that improved water flux and a high rejection was achieved. Moreover, UiO-66-PSBMA/PSf membrane exhibited excellent antifouling performance[23]. Ma et al. successfully prepared UiO-66@GO composite and polyethersulfone (PES) membrane with higher water

flux and rejection compared to polyethersulfone (PES) membrane[26]. The separation abilities of some MOF modified membranes has been shown in Table 1.

**Table 1.** Water permeability and selectivity of some MOF modified membranes

MOFs	Water flux (L m <sup>-2</sup> h <sup>-1</sup> )	Rejection rate(%)	Flux recovery ratio(%)	Ref.
TMU-5	182	-	98.74%	[24]
Zn/Co-MOF-74	>127	>92	-	[25]
UiO-66-PSBMA	602	>98	72.5	[23]
UiO-66@GO	>15	98.3	-	[26]

### 3.2. FO and nanocomposites membranes (OSN)

The nanofiltration membrane is widely used to water treatment, however, the fouling problem depressed the life of the membranes. Many works had been done to improve the antifouling property as MOFs can be successfully applied to modify the nanofiltration membrane. Makhetha et al. used (Cu(tpa))@GO to produce Cu(tpa))@GO polyethersulfone (PES) composite membranes. The nanocomposites presented high antifouling properties and exhibited selective anionic dye rejection [27]. The carboxylate functionalization of HKUST-1 modified nanofiltration membrane had positive effect on the performance of membrane which showed high rejections ( $M_w = 794$  g mol) [20]. Because the in-situ growth of ZIF-8 produced a ZIF-8 interlayer with more MOFs nanoparticles but fewer aggregates [21], the obtained PA/ZIF-8 membrane exhibited higher permanence and better selectivity than conventional PA/ZIF-8 TFN membrane.

Reverse osmosis is used to water purification processes which remains a critical issue of fouling, Yuan et al. prepared TFN-MIL-101 (Cr) membranes and found a high NaCl salt rejection achieved. Cu-BTC was also used to synthesize FO membranes. The results showed that modification process improved the antifouling properties and water flux of membrane considerably [22].

## 4. Conclusions and outlook

In conclusion, MOF/polymer hybrid membranes with higher water flux, better antifouling performance and higher protein retention have attracted more and more attention in liquid separation. The prepared MOF/polymer hybrid membranes with high hydrophilicity, excellent compatibility and unique rigidity have shown excellent separation performance. The design of new methods improve long-term stability and sharply reduce the cost will be the challenge of MOF/polymer hybrid membranes for industrial application.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (21736009, 21506193 and 21476206), Fujian Provincial Department of Education projects (grant number JAT160417) and the R&D program from Hangzhou Bureau of Quality and Technical Supervision.

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