



Nano-sized metal organic framework to improve the structural properties and desalination performance of thin film composite forward osmosis membrane



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ABSTRACT

In the present study, nano-sized metal-organic framework (MOF) particles consisting of silver (I) and 1,3,5-benzene tricarboxylic acid were synthesized and applied to improve the structural properties as well as desalination performance of thin-film composite (TFC) forward osmosis (FO) membranes. The MOF nanocrystals were incorporated into the polyamide layer of membranes through interfacial polymerization. Characterizations by Field emission scanning electron microscopy and X-ray photoelectron spectroscopy enabled the detection of MOF nanocrystals within the selective layer of the resultant membranes. The MOF incorporation led to changes of the membrane active layer in terms of hydrophilicity and transport properties, without detrimental effects on the layer selectivity. These features enhanced pure water permeability of the membranes to 129%, which was provided through 0.04% MOF loading of the organic phase during interfacial polymerization. As a result, the modified membrane exhibited an enhanced FO seawater desalination performance in comparison with the control membrane. The performance stability of TFC membrane was also improved by presence of MOF in active layer (as seen by a water flux decline of about 7% for modified membrane against about 18% for unmodified membrane when tested with real seawater). This study demonstrates the potential of MOF particles to enhance desalination performance of TFC membranes in FO systems.

1. Introduction

The continuous growth of the world population increases the water demand, leading to the rising use of alternative water sources such as desalination of seawater [1]. Technologies based on membrane processes provide an important opportunity for addressing the general water crisis by enabling water supply from different resources. Forward osmosis (FO), a high water recovery and low cost membrane-based technology, has a unique capability in desalination [2] and wastewater treatment [3–5]. Compared to pressure-driven membrane technologies, the lack of applied hydraulic pressure has been considered as advantage of FO. As a result, there are several unique benefits such as low energy consumption and low membrane fouling, as well as a high water recovery ratio [6–12]. The membrane used in FO desalination process plays the most important role as it determines the overall performance of the process. Therefore, high-performance FO membranes are highly desired. These membranes should provide a superior productivity and selectivity [13,14]. Thin film composite (TFC) mem-

branes have been used predominantly as osmotic membranes in water and energy applications because of their high intrinsic water permeability and selectivity [15–19]. Modification of TFC membranes by incorporating nanomaterials is a promising approach to further improve the membrane properties. In this regard, there are two types of strategies. A more common strategy for this purpose is to improve the substrate layer properties of TFC FO membrane, such as increasing hydrophilicity and porosity, and optimizing the pore structure, and hence reducing internal concentration polarization (ICP) [20–23]. Another approach is to improve thin active layer properties of TFC membranes. Notably, thin-film nanocomposite (TFN) membranes were developed via incorporating nanoparticles in the selective layer [24]. Various types of nanomaterials have been studied comprising zeolite, silica, carbon nanotubes, pure metals and metal oxides to improve the TFN membranes properties [25–30]. For instance, hydrophilic and negatively charged zeolite nanoparticles were loaded in the polyamide layer during interfacial polymerization process. The modification considerably enhanced the permeability and surface properties of the

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resultant membrane [24,28]. Silica nanoparticles were also used in TFC membrane for application in water purification, presenting an improved performance compared to control membrane [31,32]. Despite this progress, there is still a major problem, as incorporating nanomaterials in the membrane active layer can cause detrimental effects on the membrane selectivity [33–35].

In recent years, metal–organic frameworks (MOFs), consisting of metal ions coordinated to organic ligands as linkers, have been studied as new category of organic/inorganic hybrid materials with tailored pore structure. The organic linkers present in MOFs structure provide also a better affinity between MOF and organic polymers, compared with purely inorganic compounds as additive. That had already been utilized for preparation of advanced mixed matrix membranes [36–38]. The good compatibility between the two phases has been related to the formation of non-covalent bonds, such as hydrogen bonds, or even covalent bonds when the MOF-polymer composite is formed via in situ polymerization [38]. This feature provides an opportunity for improving the membrane active layer properties without adverse effects on its selectivity. As a result, incorporating MOFs in the active layer of TFC membranes offers to promise advantages over other nanostructured materials.

This study aims to investigate the use of MOF nanocrystals, consisting of silver (I) and 1,3,5-benzene tricarboxylic acid (3HBTc), for improving FO desalination performance of TFC membranes. Due to the organic linker in the MOF nanocrystals framework there should be a good compatibility with the aromatic polyamide layer because hydrogen bonding between 3HBTc and the polyamide is favored and even the formation of amide bonds between MOF and polyamide is possible during in situ cross-linking polycondensation. Therefore, the membrane active layer should be improved without detrimental effects on the layer selectivity. To the authors' knowledge, this is the first research incorporating MOF nanocrystals in the thin polyamide layer of TFC membranes to improve FO desalination performance.

2. Materials and methods

2.1. MOF preparation

MOF nanocrystals were synthesized via ultrasonic irradiation of the reaction mixture at a frequency of 24 kHz (Hielscher UP400s, Germany) for a reaction time of 60 min. In a typical synthesis, silver nitrate (AgNO_3 , 1g) was dissolved in 40 mL N,N-dimethylformamide (DMF) and mixed with 40 mL solution of 3HBTc (1g) in DMF. The output and pulse of ultrasonic waves were kept to be 80 W and 0.6, respectively. Subsequently, the product was centrifuged, and the precipitate was washed with a mixture of water and ethanol (1:1) and subsequently dried in an oven for 24 h at 60 °C. The obtained product was stored in a sealed container before use.

2.2. FO membranes preparation and characterization

The substrate membrane were fabricated using a dope solution containing 14 wt% polyethersulfone (PES) and 1 wt% polyvinylpyrrolidone (PVP) dissolved in DMF. The dope solution was spread onto a flat glass using casting knife set to obtain a thickness of 100 μm . The casted film was immersed into a water container at 25 °C to initiate phase inversion. The resulting PES substrates were kept in deionized (DI) water before use.

Thin film polyamide layer of FO membranes was made via interfacial polymerization (IP) process on the PES substrates. The PES substrates were dipped in a 2.0 wt% m-phenyldiamine (MPD) solution in water for 2 min. An air knife was used to remove the surplus MPD solution from the substrate surface. Then the MPD-soaked substrates were immersed in a 0.1 wt/v% trimesoylchloride (TMC) solution in n-hexane (30 s). The reaction between MPD and TMC at the interface of the two immiscible solutions formed a nanoscale polyamide

barrier layer on the PES substrates. Afterwards, the membranes were immediately transferred to an oven (80 °C) for five minutes. The resultant TFC membranes were kept in DI water before use. The previously synthesized MOF nanocrystals were loaded within the organic solution used for fabrication of polyamide layer by IP to yield thin-film nanocomposite (TFN) membranes. Three different concentrations of MOF nanocrystals (0.02, 0.04 and 0.08 wt/v%) were loaded in the TMC in n-hexane solution and dispersed by ultrasonication for 30 min. The prepared membranes are denoted as TFC (the control membrane without MOF), TFN-0.02 (membrane with nominal loading of 0.02% MOF nanocrystals), TFN-0.04 (nominal loading 0.04%) and TFN-0.08 (nominal loading 0.08%).

Field emission scanning electron microscopy (FE-SEM), with the instrument TESCAN MIRA3 equipped with an energy-dispersive X-ray spectroscopy (EDX) unit, was used to characterize the cross section and top surface morphologies and chemical compositions of the membranes. The samples were coated with a uniform gold layer before observation. Also, atomic force microscopy (AFM), with the instrument Nanosurf EasyScan II, was used to investigate the surface morphology of the prepared membranes. The most common surface roughness parameters of the membranes, including the roughness average (R_a), the root mean square roughness (R_q) and the peak to valley roughness (R_m), were calculated (for definitions and details see [Supplementary information](#)).

A contact angle instrument (G10, KRUESS) and water as test liquid were used to examine five random spots on the membrane surface in terms of hydrophilicity. The experimental error was considered via reporting the average values.

The elemental composition of the polyamide layer was identified by X-ray photoelectron spectroscopy (XPS) using an instrument from Bestec, Germany, and an Al K α X-ray source. The survey and high resolution spectra were collected with passing energy of 160 eV and 20 eV, respectively. The measured binding energies were calibrated with respect to C1s hydrocarbon signal at 284.6 eV. The element ratio of O/N was used to estimate the cross-linking degree of the polyamide layer, using the following equations [39]:

$$O/N = \frac{3m+4n}{3m+2n}, \quad m+n=1 \quad (1)$$

where m and n are the relative fractions of cross-linked part and linear part, respectively.

2.3. Transport properties and FO performance assessment

The FO water flux and reverse solute flux as the most common performance indicators for FO membranes were measured via a lab-scale FO setup. The setup contained a membrane test cell with an effective area of 30 cm^2 . Two diaphragm pumps circulated feed solution (FS) and draw solution (DS) on both sides of the cell. The setup was equipped with two adjustable flow meters to set a crossflow velocity of 21 cm/s in both the FS and DS channels. The FO setup had controllers to monitor and fix temperature of the FS and DS. DI water was used as FS in the experiments. In order to provide the osmotic gradient, different concentrations of NaCl solution (0.5, 1, 1.5 and 2 M) were used as DS. A balance monitored the weight change of FS at 60 s intervals to measure the FO water flux (J_w), calculated using the following equation:

$$J_w = \frac{\Delta m_{\text{feed}} / \rho_{\text{feed}}}{A_m \times \Delta t} \quad (2)$$

where Δm_{feed} is the weight change of FS, ρ_{feed} is the FS density, A_m is the membrane area in the cell and Δt is the time interval.

A conductivity meter was used to monitor changes in salt content of the FS at 10 min intervals to calculate the FO reverse solute flux (J_s), using the following equation:

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