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Thin Film Nanocomposite Hollow Fiber Membranes Incorporated with Surface Functionalized HKUST-1 for Highly-efficient Reverses Osmosis Desalination Process

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Abstract

A new class of thin film nanocomposite (TFN) hollow fiber (HF) membrane of polydopamine (PDA) modified HKUST-1 (mHKUST-1) incorporated in polyamide (PA) matrix supported by polyethersulfone (PES) substrate was constructed via interfacial polymerization method for brackish water desalination in low-pressure reverse osmosis (RO) process. The PDA modification facilitated the HKUST-1 even dispersion, thus resulting in better compatibility between the inorganic nanofillers and the organic matrix. The impact of HKUST-1 loadings on the overall performances of the resultant HKUST-1@PA/PES membranes was investigated. Introducing the mHKUST-1 nanofillers not only enhanced surface hydrophilicity and negative surface charges for the selective layer, which improved membrane's fouling resistance to humic acid (HA), but also led to nearly doubled water permeance when comparing with the pristine PA membrane (increasing from 3.51 to 6.94 Lm⁻²h⁻¹bar⁻¹), without obvious salt rejection deterioration (~98.2% at 2 bar and 97.4% rejections at 4 bar for 500/2000 ppm NaCl solutions, respectively). The integrity of the HKUST-1@PA/PES membrane was examined and verified after 30-days operation. Overall, the results achieved in this work demonstrate promising potential of the metal organic framework (MOF)-based TFN membranes used for desalination in low-pressure RO process. To sum up, this work has exhibited a facile method to incorporate the metal organic framework (MOF) into the PA layer, and the resultant MOF-based TFN membrane indicates its great potential for desalination in low-pressure RO process.

Key words: Thin film nanocomposite membranes; hollow fibers; metal organic framework; low-pressure reverse osmosis (RO) process; desalination.

1. Introduction

The rapid industrial development and population growth in the last decade have given rise to the ever-increasing demand for clean water access, and global water scarcity has become a critical issue. The decreasing water supply has motivated high usage of unconventional water sources (brackish water and seawater), and driven the advancement of low-cost and efficient water reclamation and desalination approaches [1]. Thin-film nanocomposite (TFN) membranes have becoming a rising star for the production of clean water through reverse osmosis (RO) process in the coming decades [2, 3]. A desired RO membrane should possess high water permeance with outstanding solute selectivity. However, very few commercialized TFN RO membrane could be currently available for the desalination process, due to the complex membrane preparation process [4]. To overcome these problems, new membrane materials that can provide enhanced performance and stability in long-term operation are still in high demand in RO applications.

By incorporation of polymers processing versatility and inorganic fillers excellent separation capability, TFN membranes produced by the embedding of inorganic fillers into the organic matrix have demonstrated good potential to break the trade-off limits of the traditional TFC membranes, since the embedded materials with lower intrinsic resistance could theoretically provide the transport channels in polymer matrix for water molecules fast passing through, while maintaining the steric hindrance toward solutes [5, 6]. Consist of inorganic metal centre or cluster interacted by organic linkers to form cage structures, metal-organic frameworks (MOFs) seems a promising inorganic-organic hybrid material to be employed in the TFN membranes [7]. MOFs have been proved its high potential to fabricate novel TFN membranes with outstanding water permeance and rejection capability, because of their porous structure and the versatile nature in building blocks and functionalities [8]. For instance, Ma et al. [9] embedded super hydrophilic Zr-MOFs of UIO-66 in thin film polyamide (PA) membrane. A significant improvement of 52% in pure water permeation (the highest flux of $51.3 \text{ Lm}^{-2}\text{h}^{-1}$ in PRO mode / $27 \text{ Lm}^{-2}\text{h}^{-1}$ in FO mode) was obtained, while maintaining a rejection of 95% for NaCl. Sorribas et al. [10] developed the TFN membranes by using the Zn-MOFs nanoparticles of ZIF-8, MIL-53(Al), NH₂-MIL-53 (Al) and MIL-101 (Cr) as fillers (50-150 nm) in the PA matrix. The membrane was also evaluated for organic nanofiltration (NF) process, where it exhibited increased permeance of $3.9 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for methanol, and $11.1 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for tetrahydrofuran, while remaining a high styrene oligomers rejection of 90%. Park et al. [11] prepared TFN PA membrane supported by polysulfone substrate incorporated with Cu-MOFs HKUST-1 nanoparticles for desalination of NaCl in RO process. Their data showed that the water flux increased with the increasing loading mass of HKUST-1 nanofillers, attributed to the increment of intrinsic porosity, so that the pure water permeability (PWP)

of $2.7 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and NaCl rejection of 96% were obtained. Although the TFN membranes are advantageous of improving the organophilicity/hydrophilicity, permeance and rejection, works about MOFs incorporated TFN membranes that can be used for highly-efficient RO desalination were rarely reported. Fabrication of such membrane is currently a prototype [12], because of two major challenges in 1) dispersing the nanoscale MOF nanofillers in an ultrathin organic matrix without apparent aggregation, and 2) avoiding the formation of nonselective interface defects between the organic matrix and MOF nanofillers [13].

To date, many efforts have been reported to address the incompatibility between inorganic fillers and organic matrix [14, 15]. Yang et al. [16] prepared the ZIF-8/PEI mixed matrix membranes (MMMs) used for nanofiltration (NF) via chelation-assisted interfacial reaction process. As a result of the superior chelating capability of polyethyleneimine (PEI) to metal ions, the resultant MMM showed an integrated structure with high rejection of 99.2% for dye removal (congo red) [17]. Zhu et al. [18] embedded hydrophilic ZIF-8 in thin film PA membrane for NF application. After modification with poly (sodium 4-styrenesulfonate), the super-hydrophilic ZIF-8 nanofillers could be well dispersed into the aqueous solutions of piperazine monomers, followed by polymerization with trimesoyl chloride (TMC), thus producing the integrated TFN membranes with high rejection of 99.9% for RB2. Researchers have demonstrated the enhancement in MMM/TFN membrane integrity by optimizing the interface compatibility between organic matrix and inorganic fillers via surface functionalization methods [19, 20]. However, to synthesize defect-free MMMs/TFN membranes with high-loading nanosized fillers in a selective layer is still limited, since it is extremely challenging to prepare evenly dispersed nanofillers without agglomeration in the polymer matrix. For example, Duan et al. [21] produced a TFN RO membrane embedded with MOF nanofillers of ZIF-8 for NaCl desalination. They found that the higher loading of ZIF-8s resulted in a decrease in NaCl rejection, and the contradictory result is possible because of the non-selective defects between ZIF-8 and PA, due to the severe aggregation of ZIF-8 fillers at a higher loading concentration of 0.4 w/v % [22, 23]. Mahdi et al. [24] also found that aggregation occurred in ZIF-8 loaded polymer matrix with the loading concentration of higher than 20 wt.%, thus resulting in MMMs separation performance deterioration. In summary, increasing the MOF fillers loading while preventing the aggregation of MOFs nanofillers throughout the organic matrix is a scientific and practical challenge for preparing highly-efficient MMMs/TFN membrane for RO applications.

Among MOF nanomaterials, HKUST-1 is extensively reported in gas separation, adsorption and catalysis, due to its excellent structural and chemical stability [25, 26]. HKUST-1 ($\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$) consists of $\text{Cu}_2(\text{H}_2\text{O})_2$ dimer clusters connected with benzene-1,3,5-tricarboxylate (H_3BTC) ligands, thus constructing a three-dimensional open framework [27]. HKUST-1 is composed of porously intersecting structure: $\sim 9 \text{ \AA}$ cavity cages interact with $\sim 5 \text{ \AA}/3.5 \text{ \AA}$ pore apertures as estimated, so that it could be inferred that the membranes developed with HKUST-1 would achieve high selectivity of water

molecules (2.8 Å) over hydrated sodium ions (7 Å) based on the size-exclusion mechanism [28]. Therefore, the HKUST-1 doped MMMs used for desalination seems promising, because of 1) theoretically fast transport of water molecules passing through the flow channels of the framework, and 2) the superior solute rejection due to the steric exclusion effects [11]. However, it is rarely reported about HKUST-1 embedded PA TFN membrane used for RO process in literature, since the HKUST-1 nanofillers are structurally unstable in the hydrothermal environment [29].

In this study, we designed and fabricated an HKUST-1 doped PA membrane via interfacial polymerization method, where the incorporated HKUST-1 nanofillers were modified with polydopamine (PDA). The highly-efficient mHKUST-1@PA/PES TFN membrane was used for brackish water desalination in low-pressure RO process. The PDA modification was employed for fabricating mHKUST-1 nanofillers without aggregation in aqueous solution. Moreover, it is also anticipated that the PDA layer could enhance the interface compatibility between inorganic nanofillers and organic matrix. The microstructures and physicochemical properties of the mHKUST-1@PA/PES membrane could be precisely tuned via the optimization of loading mass of mHKUST-1 nanofillers. The separation performances in terms of water permeance, desalination capability and long-term stability were also investigated by desalination of 500/2000 ppm NaCl aqueous solutions in RO process for 30-days operation test. Fig. 1 schematically illustrates the development of the mHKUST-1@PA/PES TFN membranes and their predicted effects in low-pressure RO application. This work aims to shed some light for the advancement of competent TFN membranes to break through the current bottleneck for brackish water desalination.

Fig. 1 Schematic illustration of the mHKUST-1@PA/PES membranes and salt removal in low-pressure RO application (HA- humic acid).

2. Experimental

2.1 Synthesis of three types of HKUST-1 nanofillers

HKUST-1 nanofillers were synthesized using a similar method described in our previous work [30]. Firstly, 1.5 g of copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Merck, 99.5%) was dissolved in 50 ml deionized water (DI water, produced by Milli-Q system, Millipore), and 0.8 g of H_3BTC (Merck, 95.0%) was dissolved in 50 ml ethanol (Ethanol absolute, VWR International, 99.98%). Then, these two solutions were mixed at room temperature and stirred for 15 min. In order to remove the unreacted H_3BTC in the solution, the HKUST-1 nanofillers were collected by centrifuging at 12000 rpm for 10 min, then rinsed by DI water. The above procedure was repeated for 3 times. After the supernatant was removed, the bottom product of wet HKUST-1 nanofillers was collected. After the drying-free preparation process, the wet HKUST-1 nanofillers were re-dispersed in an aqueous solution for subsequent PDA (Dopamine hydrochloride, Sigma-Aldrich) modification.

The PDA modification was completed by dopamine self-polymerization on the surface of HKUST-1 nanofillers. The HKUST-1 nanofillers were directly re-dispersed into dopamine (0.5 g/L) in a concentration of 5 mg/L in Tris buffer aqueous solution, followed by 2 h stirring. The PDA modified HKUST-1 nanofillers (designated as mHKUST-1) were obtained by centrifuging at 12000 rpm for 10 min, then rinsed with DI water. The above cleaning procedure was repeated for 3 times. Finally, by adding different amounts of aqueous m-phenylenediamine (MPD, ACROS OrganicsTM, 99%) solution, the mHKUST-1 nano-dispersed suspensions with different concentrations were obtained. For comparison, the drying-free HKUST-1 without PDA modification was also prepared, thus another type of suspension was prepared using the wet HKUST-1 nanofillers without PDA modification as a reference.

For further comparison, the pristine HKUST-1 powder (designated as dry HKUST-1) was also prepared. Most of the preparation procedure is the same as the suspension dispersed with mHKUST-1 nanofillers, but the major difference was that the collected nanofillers were firstly dried at 70 °C for 12 h before added into MPD aqueous solution for preparation of HKUST-1 powder based suspension, as most literature reported [11, 18, 31].

2.2 Preparation of mHKUST-1@PA/PES hollow fiber based TFN membranes

A crosslinked PA layer on the polyethersulfone (PES) home-made substrate (OD: 1.2 ± 0.01 mm; ID: 0.9 ± 0.01 mm; MWCO: 180 ± 15 kDa) was formed via interfacial polymerization, as described in literature [32, 33]. Generally, the lumen of the PES hollow fiber (HF) substrate was firstly immersed in

an MPD solution for 20 min. Cyclohexane was then used to rinse in the lumen side and remove the excessive solution on the inner surface of the membranes. Lastly, trimesoyl-chloride (Sigma-Aldrich, 98%) in cyclohexane (Merck, 99.5%) was pumped from the lumen of fibers for 3 min to form the thin layer. The produced membranes were stored in DI water for further applications.

The mHKUST-1@PA/PES membranes were prepared following the same procedure except for the addition of mHKUST-1 nanofillers in the aqueous MPD solution. The well-dispersed nanofillers was achieved by another vigorous stirring for 30 min, followed by ultrasonication treatment for 10 min. The loadings of mHKUST-1 nanofillers were varied from 6, 12, 24 and 48 dwb.% (dry weight basis of MPD), designated as mHKUST-1@PA-6/PES, mHKUST-1@PA-12/PES, mHKUST-1@PA-24/PES and mHKUST-1@PA-48/PES membranes. The wet HKUST-1 without modification based MPD suspension was designated as HKUST-1@PA-6/PES membrane.

2.3 Membrane characterizations and performance evaluation

2.3.1 Characterizations chemico-physical properties of mHKUST-1@PA/PES membranes

Dynamic light scattering (DLS, Zetasizer Nano 90, Marlvern Panalytical) measurement was conducted to obtain the particle size/particle size distribution of the dry HKUST-1 powder, and the wet HKUST-1 powders with/without PDA modification. The chemical structures of HKUST-1 based samples were characterized with attenuated total reflection-Fourier transform infrared spectrometer (ATR-FTIR, Perkin-Elmer, Spectrum One System). Powder X-ray diffraction (XRD, D8 Advance Powder, Bruker) patterns were recorded at ambient temperature. Field emission transmission electron microscopy (FE-TEM, JEM 2100 F, JEOL) was employed to examine the morphologies of HKUST-1 nanofillers at 200kv.

The mHKUST-1@PA/PES membranes were coated with platinum prior to observation of the morphology using field emission scanning electron microscope (FESEM, JSM-7600F JOEL) at 5 kV. The elemental composition of the mHKUST-1@ PA membrane was identified using energy disperse X-ray (EDX) spectroscopy. Atomic-force microscopy (AFM, XE-100, Park System) was employed to examine the microstructures of the membrane surface. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) was also conducted to investigate the chemical composition and states of different membrane samples, and the results were analyzed by CasaXPS software where the C 1s peak with the energy at 284.5 eV was used for spectral calibration.

To evaluate the surface properties of mHKUST-1@PA/PES membrane, the static water contact angles (CAs) were measured by using a goniometer (Data Physics Instruments GmbH) via the sessile

drop method. The zeta potentials of the membrane surfaces were obtained by using an electrokinetic analyzer (SurPASS Anton Paar), following the streaming potential measurement method. A NaCl solution (500 ppm) was used as the background over a pH range of 3-10.

2.3.2 Characteristics of mHKUST-1@PA/PES membrane

A lab-scale module with an effective length of 15 cm was prepared by sealing five pieces of HF membranes into a polytetrafluoroethylene (PTFE) tube with epoxy on both ends. The PWP of the membrane was characterized by the amount of water permeated through the membrane at 1 bar using DI water as feed, or estimated from the equation below:

$$J = \frac{Q}{\Delta P \times A} \quad (1)$$

where J is the specific PWP of the hollow fiber membrane ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$); Q is calculated from the volume of water passed through per unit time ($\text{L} \cdot \text{h}^{-1}$); ΔP is the applied pressure across the membrane (bar); and A represents the effective membrane area (m^2).

The salt rejection of the membranes was characterized by pressurizing the membranes under 2/4 bars with 500/2000 ppm NaCl solutions using a cross-flow setup [34], respectively. The solute rejection was estimated based on the conductivity (measured by Ultrameter IITM 4P, Myron L Company) difference between the feed and permeate solution, or expressed in the equation:

$$R(d) = \frac{C_f - C_p}{C_f} \quad (2)$$

A 200 ppm humic acid (HA, Sigma-Aldrich) solution was also used as feed for mHKUST-1@PA/PES membrane filtration experiment at 2 bar. The HA rejection of the membranes was also calculated using the above equation where the concentration of the membrane was measured by a total organic carbon analyzer (TOC-VSCH, Shimadzu, Japan).

2.3.3 Characterization of antifouling properties of mHKUST-1@PA/PES membranes

HA, recognized as a common foulant during the RO process[35], was selected for the anti-fouling property tests for the mHKUST-1@PA/PES membranes. The extent of the fouling on the RO membranes was estimated by the difference between the membrane flux using different feed solutions. The RO membranes were conditioned with DI water for 30 mins to obtain a stable water flux, J_1 ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$). The feed solution was then changed to 200 ppm HA solution. The RO membranes were conditioned at 1 bar for 60 min to obtain the HA solution flux, J_p ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$). Lastly, DI water was used to rinse the RO membrane for another 30 min to obtain the water flux of cleaned membranes, J_2 ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$).

²·h⁻¹). Two cycles of the above filtration test were conducted to characterize the anti-fouling properties of the membranes.

The extent of the fouling could then be estimated by the fouling ratio (F_r) and the flux recovery ratio (F_{rr}), which are defined as follows:

$$F_r = \left(1 - \frac{J_p}{J_1}\right) \times 100\% \quad (3)$$

$$F_{rr} = \frac{J_2}{J_1} \times 100\% \quad (4)$$

where F_r represents the degree of total flux loss caused by membrane fouling. And the ratio of reversible and irreversible fouling could thus be estimated by the equations below,

$$R_r = \left(\frac{J_2 - J_p}{J_1}\right) \times 100\% \quad (5)$$

$$R_{ir} = \frac{J_1 - J_2}{J_1} \times 100\% \quad (6)$$

where R_r and R_{ir} represent reversible and irreversible fouling ratios, respectively.

3. Results and discussions

3.1 PDA modification on HKUST-1 nanofillers

The HKUST-1 nanofillers were modified by an ultrathin PDA layer. It is well acknowledged that PDA molecules tend to achieve the wrapping on nanoparticle surfaces in a precisely controlled manner at the nano-level scale [36]. After surface modification with PDA, the nanofillers could be uniformly dispersed in water at least 6 h, suggesting that the nanofillers had better colloidal stability with smaller or narrower particle size and particle size distribution of ~100 nm without aggregation in comparison with the dry HKUST-1 nanofillers, as shown in Fig. 2 (a) and (b). The well dispersed mHKUST-1 crystals without drying process is a vital factor to produce the nanoscale uniform, defect-free and highly permeable TFN membranes, which will be discussed in 3.2.1.

To further examine the physical, chemical and structural properties of PDA layer, the HKUST-1 nanofillers were examined by various characterization techniques. Fig. 2 (c) exhibits the FTIR spectra of pristine dry HKUST-1, wet HKUST-1 and mHKUST-1 nanofillers. The FTIR spectrum of pristine HKUST-1 matches well with the previous literature [37]. The FTIR spectrum of wet HKUST-1 and mHKUST-1 nanofillers are generally consistent with the pattern of pristine HKUST-1 nanofillers, suggesting that PDA modification may not impact its chemical structure significantly. However, for the mHKUST-1 nanofillers, the new vibrational absorption band at stretching frequency of 1050 and 1250

cm^{-1} are assigned to $-\text{NH}$, that is attributed to the out-of-plane bending absorption of amine groups from dopamine [38, 39]. Moreover, by comparison with the wet HKUST-1 nanofillers without PDA modification, it is visible that there is a significant increase in 1370 cm^{-1} band for the mHKUST-1 nanofillers. The effect can be related to the π - π stacking incorporated with van der Waals interaction on HKUST-1 nanofillers, involving the aromatic core structures of the dopamine molecules [40, 41]. These results provide evidence for the interaction between dopamine and the HKUST-1 nanofillers. Besides, XRD patterns of pristine HKUST-1, wet HKUST-1 and mHKUST-1 are in agreement with the pattern in literature [42], where the results have shown the excellent nanocrystal structure and imply that PDA modification has no apparent influence on the inherent nanostructure of HKUST-1 nanofillers. To sum up, it could be concluded that the HKUST-1 nanofillers were well synthesized, and the PDA modification was done successfully.

Fig. 2 Comparisons of (a) photo images of the aqueous suspension, (b) particle size distribution, (c) XRD pattern, and (d) FTIR pattern of dry HKUST-1, wet HKUST-1 and mHKUST-1.

In order to visually investigate the morphologies of the nanofillers, TEM images of pristine dry HKUST-1 powder, wet HKUST-1 and mHKUST-1 nanofillers are shown in Fig. 3. Fig. 3(a) displays the pristine dry HKUST-1 nanofillers, and the particles with an average diameter of $\sim 200 \text{ nm}$ are observed. The enlarged TEM image illustrates a relatively larger particle composed of smaller nanoparticles with clear crystal lattice fringes, further indicating that the well-crystalline HKUST-1 is synthesized [43]. For the wet HKUST-1 nanofillers without PDA modification, the particles with an

average diameter of ~40 nm are observed. However, some precipitation and aggregation of 80 nm particles can also be observed, as shown in Fig. 3(b). This can be explained that the HKUST-1 nanofillers is likely to aggregate in suspension as a result of their high surface tensions [13]. For the mHKUST-1 nanofillers, the uniformly dispersed particles with an average diameter of ~20 nm could be observed, and the better dispersion could be ascribed to the steric hindrance of PDA layer, as shown in Fig. 3(c). Moreover, the enlarged TEM image illustrates the apparent crystal lattice fringes, further confirming that the PDA modification not only has no adverse effect on the HKUST-1 nanofillers crystallization, but also overcomes or minimizes the f HKUST-1 nanofillers aggregation. The resultant mHKUST-1 nanofillers was selected for further studies, because of their better dispersion performance without physicochemical properties deterioration.

Fig. 3 TEM images of (a) dry and (b) wet HKUST-1 nanofillers, and (c) mHKUST-1 nanofillers.

3.2 Physicochemical characterizations of mHKUST-1@PA/PES membranes

3.2.1 Morphologies and microstructures of mHKUST-1@PA/PES membranes

In order to inspect the morphologies and microstructures of the newly developed mHKUST-1@PA membranes with different mHKUST-1 additions, FESEM incorporated with EDX characterizations were carried out, as in Fig. 4. Fig. 4(a) shows a “ridge-and-valley” surface structure for the PA membrane without HKUST-1 nanofillers doping. A possible explanation about such morphology is as follows: the underlying PES substrate has a relatively hydrophobic surface, so that the MPD aqueous solution tend to be constrained without spreading during the superficially drying process. When MPD from aqueous phase and TMC from the solvent phase crosslink with each other at the solvent-aqueous interface, the MPD tends to migrate quickly into the solvent phase and resulted in the growth of polyamide tufts in the direction perpendicular to interface, eventually giving rise to roughly crumpled structures because of the inner crosslinking reaction [44]. By doping the mHKUST-1 nanofillers from 6 to 24 dwb%, a smoother surface with less pronounced “ridge-and-valley” structure is found. Moreover, with higher mHKUST-1 nanofillers loadings, more nanofiller features are observed on the surface, which may imply that mHKUST-1 nanofillers are incorporated in continuous PA layer, as shown in Fig. 4 (b), (c) and (d). The surface morphology change by adding mHKUST-1 nanofillers is likely attributed to that the amphiphilic mHKUST-1 nanofillers not only facilitates the adsorption of a certain amount of hydrophilic MPD monomers, but also tends to anchor on the PES substrate. Therefore, the pre-deposited mHKUST-1 was able to keep more MPD on the PES substrate, thus enhanced the interfacial polymerization reaction, and consequently formed a relatively smoother surface structure [18]. By continuously increasing the mHKUST-1 nanofillers doping amount to 48 dwb% (Fig. 4(d)), the agglomeration of larger mHKUST-1 particles is observed. The larger nanofillers incorporated mHKUST-1@PA membranes may cause the deterioration of salt retention capability, which will be discussed later (section 3.3). The effect of the PDA modification on mHKUST-1@PA/PES membrane microstructures was also analyzed by examining the surface morphologies of HKUST-1@PA-24/PES membrane without PDA modification, as shown in Fig. 4(e). When compared with the mHKUST-1@PA-24/PES membrane, the HKUST-1@PA-24/PES membrane exhibited some defects and cracks around the embedded nanofillers, and this could be likely ascribed to the weak affinity between inorganic nanofillers and organic matrix [45]. This result further proves that the PDA modification, as the interfacial linker between the HKUST-1 nanofillers and PA matrix, is prerequisite for preparing decent TFN membranes [46]. Therefore, the mHKUST-1@PA-24/PES membrane was selected for further studies because it has the best dispersed HKUST-1 nanofillers embedded in PA matrix without interfacial defects and cracks.

Fig. 4 FESEM surface images of (a) pristine PA/PES membrane, (b) mHKUST-1@PA-6/PES membrane, (c) mHKUST-1@PA-24/PES membrane, (d) mHKUST-1@PA-48/PES membrane and e) HKUST-1@PA-24/PES membrane without PDA modification.

The surface microstructure investigation on mHKUST-1@PA membranes with different mHKUST-1 nanofillers doping amounts was conducted (Fig. 5). The pristine PA membrane has an R_{rms} (root mean square roughness) of 89.6 nm and R_a (average roughness) of 72.5 nm, showing a ridge-and-valley structure (Fig. 5(a)). After incorporated with mHKUST-1 nanofillers of 24 dwb%, a smoother surface with less pronounced ridge-and-valley morphology (R_{rms} of 57.2 nm, and R_a of 44.3 nm) is obtained. Moreover, some “cubic” features can also be observed on the surface, which are most likely mHKUST-1 nanofillers embedded in the PA layer, as exhibited in Fig. 5(b). By continuously increasing the mHKUST-1 nanofillers mass to 48 dwb%, more apparent “cubic” features with larger size appear, which result in the surface layer becoming rougher with R_{rms} of 64.8 nm and R_a of 51.1 nm, as exhibited in Fig. 5(c). The TFN membrane surface morphology with less “ridge-and-valley” structure is also illustrated in AFM images, which is in agrees well with the results obtained from the SEM images, as shown in Fig. 4.

Fig. 5 AFM characterizations of (a) pristine PA/PES membrane, (b) mHKUST-1@PA-24/PES membrane and (c) mHKUST-1@PA-48/PES membrane.

The FESEM characterizations on the cross-section of pristine PA and mHKUST-1@PA-24/PES membranes were also applied to further evaluate the effect of mHKUST-1 nanofillers loading on the morphology throughout the PA layer. For the pristine PA membrane (Fig. 6(a)), the pristine PA layer (~ 200 nm) presents a dense and crumpled structure. For the mHKUST-1@PA-24 membrane (Fig. 6(b)), it also exhibits the homogeneous layer with a thickness of ~ 200 nm, where some embedded HKUST-1 nanofillers could be observed. This could suggest the HKUST-1 nanofillers are successfully embedded in the PA matrix layer through the IP process.

Fig. 6 FESEM cross-section images of (a) pristine PA/PES membrane, and (b) mHKUST-1@PA-24/PES membrane.

EDX mapping characterization was performed to further monitor the HKUST-1 nanofillers distribution in mHKUST-1@PA-24/PES membranes, shown in Fig. 7. It can be observed that the Cu elemental map showed uniform dispersion of HKUST-1 throughout the membrane surface, as demonstrated in Fig. 7(a). For the cross-section results, as shown in Fig. 7(b), there is an obvious transition of Cu between the mHKUST-1@PA layer and the PES substrate, further verifying that the mHKUST-1 nanofillers are uniformly embedded in the PA selective layer without severe infiltration into PES substrate.

Fig. 7 EDX-mapping characterizations on (a) surface and (b) cross-section of mHKUST-1@PA-24/PES membrane.

3.2.2 Surface properties of mHKUST-1@PA/PES membranes

The surface hydrophilicity of mHKUST-1@PA/PES membranes with different mHKUST-1 nanofiller doping amounts was measured, as in Fig. 8(a). The relatively hydrophobic PES substrate exhibits a CA of 75° , while the CA decreases to 51° after the deposition of PA layer covering the surface of PES substrate. By continuously loading the mHKUST-1 nanofillers, the surface hydrophilicity of mHKUST-1@PA/PES membranes is improved where the CA decreases from 51° to 34° , and this can be attributed to the mHKUST-1 nanofillers with better polar amine ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) groups on the membrane surfaces that enhance the water wettability compared to the pristine PA membranes [11]. To study the mHKUST-1@PA/PES membrane surface charge properties, zeta potential measurements were conducted, as shown in Fig. 8(b). There is a trend for the surface charge to decrease with an increasing amount of HKUST-1 nanofillers doping, owing to the stronger negative charge caused by the carboxyl groups from the hydrolysis of H_3BTC linker. Therefore, more negative zeta potential values were obtained because more mHKUST-1 nanofillers were introduced, thus resulting in the more negatively charged mHKUST-1@PA/PES membranes. In conclusion, the introduction of mHKUST-1 nanofillers improves the PA layer's hydrophilicity and makes the membrane more negatively charged.

Fig. 8 Comparisons of (a) surface hydrophilicity and (b) zeta potentials of pristine PA/PES, mHKUST-1@PA-6/PES, mHKUST-1@PA-24/PES and mHKUST-1@PA-48/PES membranes.

3.2.3 Chemical compositions of mHKUST-1@PA/PES membranes

In order to understand the chemical compositions and bonding mechanism of mHKUST-1 nanofillers with PA matrix, XPS test was carried out and the spectra were presented in Fig. 9. Fig. 9(a) shows that there is no obvious signal of Cu element on the pristine PA membrane surface. Meanwhile, for the mHKUST-1@PA/PES membrane, two peaks of divalent Cu^{2+} located at 934.6 eV and 954.4 eV were observed, which is corresponded to $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$, respectively. Nonetheless, the “shake-up satellites” (which are the other peaks located in the range of 930~965 eV except for the two peaks of 934.6 eV and 954.4 eV) found in Cu spectra could be a good indicator for the existence of Cu^{2+} [47, 48]. Meanwhile, the peak of C 1s that consists of three peaks appeared at 284.1, 287.4 and 290.8 eV was detected, corresponding to the C-C, C-N, and C=O, respectively, as exhibited in Fig. 9 (b) [49]. Comparing to the spectra of mHKUST-1@Pa/PES membrane and that of the pristine PA membrane, the peak intensity of C-N and C=O was found to increase, and this could be ascribed to the amino and carboxylic groups from PDA modified HKUST-1 nanofillers.

A possible formation mechanism of the top layer of the mHKUST-1@PA/PES membrane could thus be proposed: an interface between the organic PA matrix and inorganic HKUST-1 nanofillers is constructed through PDA coating, where the interfacial interaction of the amine groups from PDA/PA molecules and the carboxylic groups from HKUST-1 nanofillers is introduced via hydrogen bonding [46]. Therefore, the PDA modification is favourable for the compatibility improvement between the inorganic HKUST-1 nanofillers and organic PA matrix, as schematically shown in Fig. 1.

Fig. 9 The XPS spectra of (a) Cu 2p and (b) C 1s on mHKUST-1@PA/PES membrane and pristine PA/PES membrane; and the corresponding curve fittings of mHKUST-1@PA/PES membrane.

3.3 Performance of mHKUST-1@PA/PES membranes in low-pressure RO application

3.3.1 Separation performance of the mHKUST-1@PA/PES membranes

We evaluated the separation performance of the mHKUST-1@PA/PES membranes used for brackish water desalination in low-pressure RO process, where the separation performance can be evaluated in terms of the PWP, and the salt rejection of NaCl solutions (500/2000 ppm, respectively), as shown in Fig.10. In Fig. 10 (a), for the mHKUST-1@PA/PES membranes, however, PWP and salt rejection increase with the increase of mHKUST-1 nanofillers loading amount from 6 to 24 dwb%. For instance, by comparison with the PWP and salt rejection of pristine PA/PES composite membrane (PWP of $3.72 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, and rejection of 97.1/95.8% for 500/2000 ppm NaCl solutions, respectively), the mHKUST-1@PA-24/PES membrane exhibits a significant enhancement in PWP of $7.17 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and the salt rejection of 98.2/97.4% for 500/2000 ppm NaCl solutions, respectively. The increase in both PWP and salt rejection can be ascribed to the synergistic effects as follows: 1) the increase of PWP is most likely due to the lower intrinsic resistance of the embedded mHKUST-1 nanofillers with nanoporous channels that let the water molecules fast passing through than that of the relatively denser PA matrix; 2) the higher hydrophilicity of mHKUST-1@PA membranes can lead water molecules to be easier absorbed into an organic matrix, thus facilitating water transport through the porous channels; 3) the increased separation performance could also be attributed to the stronger negative charge of the

membranes induced by mHKUST-1 nanofillers [11, 21, 31]. However, the higher salt concentration of 2000 ppm also results in the rejection deterioration as shown in Fig. 10 (a), and this should be ascribed to the more severe concentration polarization (CP) phenomenon. Moreover, the severe CP led to elevated salt concentration near the membrane surface and lower permeate flux, so that results in a lower apparent salt rejection [50, 51]. By continuously increasing the mHKUST-1 doping mass to 48 dwb%, however, the PWP of mHKUST-1@PA/PES membrane increased to $8.3 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ while the salt rejection decreased to 71.6% and 68.8% for 500/2000 ppm NaCl solutions, respectively, because of the formation of non-selective interface defects caused by the aggregated mHKUST-1 nanofillers, which further indicates that the optimum dosage of mHKUST-1 addition is 24 dwb%.

Fig. 10 Comparisons of (a) PWP and NaCl (500/2000 ppm) rejection of mHKUST-1@PA/PES membranes with different MOFs doping amounts, and (b) long-term performance of PWP and NaCl (500 ppm) rejection of pristine PA/PES composite membrane and mHKUST-1@PA/PES membrane.

Compared with the state-of-the-art desalination performances of MMMs or TFN membranes in RO applications from literature, the mHKUST-1@PA/PES membrane fabricated in this work exhibited competent performance including PWP with a high rejection of NaCl, as shown in Table 1. The results could be elucidated by 1) the hydrophilicity of the doped mHKUST-1 nanofillers that could induce more water molecules easily be absorbed and transported through the MOFs' lower mass-transfer-resistance pathways; 2) structurally unstable nature of the doped mHKUST-1 nanofillers may be decomposed during the filtration test that creates additional intrinsic nanopores or voids for increased water molecules transport through the PA matrix layer.

Table 1. Overall comparison of separation performances on various MMMs or TFN membranes

Membrane materials	Structure	Membrane thickness (nm)	PWP ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	Rejection (%)	Reference
PA@UiO-66	Flat sheet (FS)	603	3.33	95.4 (1000 ppm NaCl, 2 bar)	[9] , 2017
PA/PSF@HKUST-1	FS	29	2.73	96 (2000 ppm NaCl, 17.5 bar)	[11], 2017
PA@ZIF-8	FS	N.A.	14.90	12 (1000 ppm NaCl, 4 bar)	[18], 2017
PA@ZIF-8	FS	N.A.	3.35	98.5 (2000 ppm NaCl, 15.5 bar)	[21], 2015
TFN@UiO-66	FS	100	11.5	30 (1000 ppm NaCl, 10 bar)	[31], 2017
PA/ZIF	FS	200	2.74	45 (1000 ppm MgSO_4 , 10 bar)	[52], 2015
PA@NaX-zeolite	FS	282	2.81	60 (2000 ppm NaCl, 12 bar)	[53], 2011
mHKUST-1@PA	HF	200	6.94	98.2 (500 ppm NaCl, 2 bar)	This work
mHKUST-1@PA	HF	200	6.94	97.6 (2000 ppm NaCl, 4 bar)	This work

The long-term stability test of the developed mHKUST-1@PA-24/PES membrane was carried out for brackish water desalination (500 ppm NaCl solution) in low-pressure RO process for 30 days, as shown in Fig. 9(b). According to this result, the mHKUST-1@PA-24/PES membrane exhibits a steady performance with high PWP of $6.94 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and high NaCl rejection of 97.8% (500 ppm) throughout the whole examining period, nearly doubled high that of the pristine PA membrane with PWP of $3.46 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and NaCl rejection of 97.3%. Furthermore, it should be noted that the PWP of mHKUST-1@PA-24/PES membrane increased from the beginning value of 5.7 to $6.9 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ during the first 4-days test, and this is possible because of the mHKUST-1nanofillers decomposing due to the hydrolysis of Cu-O bond in water-exposed RO process [29, 54]. However, for the rest 25-days test, the high PWP and salt rejection are remained without declining, suggesting that the IP layer can preserve the integrated surface structure that no defects generated in the membrane. Therefore, this superior stability reveals the sound structural integrity of mHKUST-1@PA/PES membranes under the current testing condition for at least 30-days continuous operation.

3.3.2 Antifouling performance of the mHKUST-1@PA membranes

The fouling resistance of the PA/PES composite membrane and mHKUST-1@PA-24/PES membrane were characterized by filtration of the HA solution. A sudden flux reduction for the pristine PA/PES composite membrane could be observed in Fig. 11, and the fouling ratio (F_f) of ~24.6% may imply that a large portion of HA has deposited onto the membrane surface. In contrast, the mHKUST-1@PA-24/PES membrane shows a milder flux deterioration, with a F_f of ~15%. Moreover, the DI water rinsing seems more effective for the mHKUST-1@PA-24/PES membrane as a flux recovery ratio (F_{rr})

of ~ 96.7% is obtained, compared to that of the pristine PA/PES composite membrane (~86.7%). The pristine PA layer presents a higher R_{ir} of 14.9% compared with that (3.3%) of the mHKUST-1@PA-24 layer. In contrast to the pristine PA/PES composite membrane, the mHKUST-1@PA/PES membrane performs a better fouling resistance against HA, while maintaining the same retention capability (~99.9%) without deterioration.

Surface microstructure, hydrophilicity and charge are important factors for determining the fouling behaviours. By comparison with the pristine PA/PES composite membrane, the better fouling-resistant property of mHKUST-1@PA/PES membrane can be ascribed to the synergistic effects of 1) the less “ridge-and-valley” and smother surface microstructure, 2) the better surface hydrophilicity and 3) the strongly negative surface charge. The mentioned properties of mHKUST-1@PA layer would promote the formation of a stable hydration layer combined with negative charges on the membrane surface, so that the interaction between the foulant and surface was weakened, resulting in less deposition of HA molecules and thus enhanced fouling resistance [35, 55].

Fig. 11 Antifouling performance of the pristine PA/PES composite membrane and HKUST-1@PA membranes: (a) time-dependent flux; and (b) fouling characteristics of membranes with two cycles of HA solution filtration tests.

4. Conclusions

The mHKUST-1@PA/PES TFN membrane was prepared via interfacial polymerization method, incorporated with interfacial modification using dopamine. As confirmed by a series of characterizations, the PDA modification of HKUST-1 nanofillers was found to be not only effective for dispersing mHKUST-1 nanofillers in the MPD solution, but also bridging the inorganic HKUST-1 nanofillers and organic PA matrix. The surface microstructures of mHKUST-1@PA membrane can be

well tuned by adjusting the amounts of doped mHKUST-1 nanofillers. The produced membrane exhibited a high PWP of $6.94 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, and high rejection of 98.2% at 2 bar and 97.4% at 4 bar for desalination of 500/2000 ppm NaCl solution, respectively, showing a significant enhancement in contrast to the pristine PA membrane separation performance (PWP of $3.46 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, and rejection of 97.1% and 95.8% for 500/2000 ppm NaCl solutions, respectively). The long-term performance of mHKUST-1@PA membrane was examined for 30-days continuous operation, and the membrane was as durable as the pristine PA/PES composite membrane. The introduction of mHKUST-1 also improved the surface hydrophilicity, as well as the negative surface charge, thus the mHKUST-1@PA membrane showed a better fouling resistance to HA while maintaining the same retention capability. Overall, the mHKUST-1@PA/PES TFN membrane developed in the current study shows a superior performance compared to most of the state-of-the-art membranes for desalination from brackish water via RO process.

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Fig. 1

Fig. 1 Schematic illustration of the TFN mHKUST-1@PA/PES membranes and salt removal in low-pressure RO application (HA- humic acid).

Fig. 2.

Fig. 2 Comparisons of (a) photo images of the aqueous suspension, (b) particle size distribution, (c) XRD pattern, and (d) FTIR pattern of dry HKUST-1, wet HKUST-1 and mHKUST-1.

Fig. 3.

Fig. 3 TEM images of (a) dry and (b) wet HKUST-1 nanofillers, and (c) mHKUST-1 nanofillers.

Fig. 4.

Fig. 4 FESEM surface images of (a) pristine PA/PES membrane, (b) mHKUST-1@PA-6/PES membrane, (c) mHKUST-1@PA-24/PES membrane, (d) mHKUST-1@PA-48/PES membrane and e) HKUST-1@PA-24/PES membrane without PDA modification.

Fig. 5.

Fig. 5 AFM characterizations of (a) pristine PA/PES membrane, (b) mHKUST-1@PA-24/PES membrane and (c) mHKUST-1@PA-48/PES membrane.

Fig. 6.

Fig. 6 FESEM cross-section images of (a) pristine PA/PES membrane, and (b) mHKUST-1@PA-24/PES membrane.

Fig. 7.

Fig. 7 EDX-mapping characterizations on (a) surface and (b) cross-section of mHKUST-1@PA-24/PES membrane.

Fig. 8.

Fig. 8 Comparisons of (a) surface hydrophilicity and (b) zeta potentials of pristine PA/PES, mHKUST-1@PA-6/PES, mHKUST-1@PA-24/PES and mHKUST-1@PA-48/PES membranes.

Fig. 9.

Fig. 9 The XPS spectra of (a) Cu 2p and (b) C 1s on mHKUST-1@PA/PES membrane and pristine PA/PES membrane; and the corresponding curve fittings of mHKUST-1@PA/PES membrane.

Fig. 10.

Fig. 10 Comparisons of (a) PWP and NaCl (500/2000 ppm) rejection of mHKUST-1@PA/PES membranes with different MOFs doping amounts, and (b) long-term performance of PWP and NaCl (500 ppm) rejection of pristine PA/PES composite membrane and mHKUST-1@PA/PES membrane.

Table 1. Overall comparison of separation performances on various MMMs or TFN membranes

Membrane materials	Structure	Membrane thickness (nm)	PWP ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	Rejection (%)	Reference
PA@UiO-66	FS	603	3.33	95.4 (1000 ppm NaCl, 2 bar)	[9] , 2017
PA/PSF@HKUST-1	FS	29	2.73	96 (2000 ppm NaCl, 17.5 bar)	[11], 2017
PA@ZIF-8	FS	N.A.	14.90	12 (1000 ppm NaCl, 4 bar)	[18], 2017
PA@ZIF-8	FS	N.A.	3.35	98.5 (2000 ppm NaCl, 15.5 bar)	[21], 2015
TFN@UiO-66	FS	100	11.5	30 (1000 ppm NaCl, 10 bar)	[31], 2017
PA/ZIF	FS	200	2.74	45 (1000 ppm MgSO_4 , 10 bar)	[52], 2015
PA@NaX-zeolite	FS	282	2.81	60 (2000 ppm NaCl, 12 bar)	[53], 2011
mHKUST-1@PA	HF	200	6.94	98.2 (500 ppm NaCl, 2 bar)	This work
mHKUST-1@PA	HF	200	6.94	97.6 (2000 ppm NaCl, 4 bar)	This work