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Hollow mesoporous silica nanoparticles: A peculiar structure for thin film nanocomposite membranes

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ABSTRACT

Incorporation of nanomaterials into the thin film composite (TFC) membrane is a promising approach to enhance the filtration performance of the membranes. This study was aimed to fabricate a novel thin film nanocomposite (TFN) membrane hybridized with hollow mesoporous silica nanoparticles (HMSN). It was expected that the HMSN-TFN membranes could have enhanced desalination performance. The research was focused on understanding of how the HMSN incorporation could affect physicochemical properties and permeation behavior of the HMSN-TFN membranes. Spherical HMSN with an average particle size of ~70 nm were fabricated by hydrothermal synthesis using soft templates. The HMSN were successfully incorporated into the selective polyamide layer in the TFN structures. The physicochemical properties of the HMSN and TFN membranes were systematically investigated using DLS, TGA, ATR-FTIR, SEM, TEM, nitrogen sorption analyser, tensiometer and XPS analysis. The HMSN-TFN membranes were more hydrophilic and performed highly improved water flux (~40%) compared with the TFC membranes, while their rejection to NaCl was not significantly changed. The HMSN-TFN membranes also displayed a higher compaction resistance than the TFC membrane, suggesting a positive interaction between the HMSN and the polyamide thin film layer. This interaction is beneficial for enhancing the strength and durability of the newly developed HMSN-TFN membranes in the high-pressure filtration process.

1. Introduction

Nowadays, thin film composite (TFC) membranes have attracted increasing interests in research towards application for desalination and water treatment processes. There is an on-going need to advance the TFC membranes with enhanced performance and physicochemical properties for desalination processes [1–3]. The advancement of nanotechnology has opened new frontiers in the development of high-performance TFC membranes. Incorporation of nanoparticles into the TFC membranes to fabricate thin film nanocomposite (TFN) membranes has been proven as a promising approach to improve the physicochemical properties (hydrophilicity, thermal resistance, mechanical stability, etc.) and permselectivity [4–7]. The most commonly used nanomaterials in the TFN fabrication include zeolite [5,8–10], silica [11–15], titania [16–18], silver [19,20], carbon nanotube (CNT) [6,21,22] and graphene oxide [23,24]. The introduction of porous nanomaterials into the thin film polyamide (PA) layer of TFC membranes has received considerable attention recently due to their unique properties and potential to improve the permeability of the TFN membranes.

The microporous (e.g. zeolite) and mesoporous (e.g. mesoporous silica) materials contain interconnected pores which are spanned through the whole structure and provide high surface area and porosity for the water molecules to pass through. Zeolites have excellent molecular sieving properties due to their small pore sizes. However, controlling their distribution and permeation pass is challenging due to their irregular cubic structure and oriented pores [25]. CNTs can be tuned from around 1.1–1.4 nm in diameter for fabricating CNT hybridized TFN membrane with improved water permeability without sacrificing the salt rejection [26]. However, CNTs' alignment to achieve the best performance can be a challenge [27]. Mesoporous silica nanoparticles (MSN) appear more dispersible than zeolites or CNTs because of their regular spherical morphology. MSN have a uniform and non-oriented distribution of pores, high specific surface area, and high thermal and mechanical properties together with a hydrophilic nature, making them widely used in the membrane separation processes such as gas separation [28–30], ultrafiltration [31], and desalination [14,25]. For instance, Bao et al. fabricated MSN (pore size: 2.47 nm) incorporated TFN membranes, which showed an improved water permeability without a noticeable change of the salt rejection [25].

Hollow mesoporous silica nanoparticles (HMSN) have exceptional and flexible porosity, high surface area and biocompatibility,

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and low density [32,33]. They have attracted considerable attention in various applications such as drug storage and delivery, high-performance catalysis and biomolecule separations [33–35]. Modulation of the hollow cavity size and the mesoporous shell thickness of HMSN provides a better control over its surface area to pore volume ratio compared to that in MSN [33]. Technically, water molecules can enter the internal cavity of the HMSN more easily than being non-specifically adsorbed on the pore walls, making the HMSN superior to the MSN for fabricating TFN membranes. However, to the best of our knowledge, no study on the incorporation of HMSN into the TFC membranes appears to be reported. It is expected that the introduction of the HMSN can facilitate the mass transfer process and improve the water permeability of the resulting TFN membranes.

Herein, this study was to fabricate HMSN incorporated TFN membrane with improved desalination performance. The hydrophilic hollow mesoporous silica nanoparticles were synthesized using a hydrothermal method using poly-(tert-butylacrylate) (PtBA) as a core template and cetyltrimethylammonium bromide (CTAB) as a structure-directing agent, followed by extraction of the simultaneous templates. HMSN were then dispersed in an aqueous monomer solution. The HMSN-TFN membranes were then prepared by the interfacial polymerization between the prepared aqueous phase containing HMSN and an organic monomer solution. Our results from bench scale desalination system investigations showed that the incorporation of HMSN into the TFC membranes at the optimum concentration can significantly improve the water flux without significant alteration of their salt rejection capability. Moreover, the HMSN-TFN membranes showned improved compaction resistance for desalination application.

2. Experimental

2.1. Materials

Polyether sulfone support (PES-MQ-50 kDa) was obtained from Synder filtration (USA). 1, 3-phenylenediamine (MPD > 99%), 1, 3, 5-benzenetricarbonyl trichloride (TMC, 98%), n-hexane, tetraethyl orthosilicate (TEOS > 99%), tert-butyl acrylate (tBA, 98%), cetyltrimethylammonium bromide (CTAB > 96%) and ammonium nitrate (NH_4NO_3) were purchased from Sigma-Aldrich. Potassium persulfate (KPS) was supplied from Chem-Supply. Sodium chloride (NaCl) and aqueous ammonia solution (28%) were purchased from VWR International. The deionized water was from a Millipore purification system.

2.2. Fabrication of HMSN

Nanoparticles were fabricated by modification of the Jiao et al.'s method [33]. The core templates were fabricated using the emulsion polymerization approach. Two g CTAB was mixed with 89 ml milli-Q water in a 3-neck flask. Two ml tBA was then added to the solution. The mixture was stirred using a mechanical stirrer rotating at 250 rpm under nitrogen protection for 1 h to remove the dissolved oxygen. The temperature was then raised to 60 °C. Five ml KPS solution (0.08 M) was injected into the degassed solution followed by adding another 10 ml tBA over a 2 h period using a syringe pump. The reaction was then allowed to continue for another 3 h at the same temperature and stirring rate. The obtained PtBA emulsion was dialyzed against the milli-Q water for 6 days using a dialysis membrane (MWCO 12–14 kDa) with the daily change of the milli-Q water.

To synthesize the HMSN, a volume of the purified emulsion containing 120 mg PtBA was added to the mixture of 80 ml milli-Q water and 40 ml ethanol. A homogeneous solution of 0.6 g CTAB in 40 ml milli-Q water was then added to the mixture. After vigorous stirring for 1 h at 40 °C, 1.4 ml ammonia solution (28%) and 2.4 ml TEOS were quickly injected into the mixture. The reaction was allowed to continue for 24 h at the same temperature and stirring rate. The obtained nanoparticles were washed several times with water and ethanol to remove unreacted residuals. The purified product is noted as HMSN-b in this study. The HMSN-b were then added to an ammonium nitrate ethanol solution (10 mg/ml) and stirred at 80 °C under reflux for 1 h to remove the PtBA and CTAB templates, forming HMSN. The obtained HMSN were centrifuged at 4000 rpm and washed with ethanol and milli-Q water for three times, and were finally redispersed in the milli-Q water for the further experiments.

2.3. Fabrication of TFC and TFN membranes

TFC membranes were fabricated using the interfacial polymerization approach with an ultrafiltration PES as the supporting layer. In detail, PES support was clamped inside a frame between an acrylic plate and a rubber gasket. The thin PA layer was fabricated on the PES support using 2% (w/v) MPD-water and 0.1% (w/v) TMC-hexane solutions. The MPD solution was first poured inside the frame, maintained for 10 min and then drained. A soft rubber roller was used after MPD soaking to remove the extra solution. The TMC organic solution was then poured into the frame and allowed to react with the surface adsorbed MPD for 1 min. The excess TMC solution was then immediately removed and the membrane was cured in the oven at 60 °C for 10 min. The resulting TFC membranes were subsequently washed with 22 °C distilled water and stored wet at 5 °C for the further characterization and evaluation. The TFC membrane is noted as the control membrane in this study, where the HMSN incorporated TFC membranes are noted as TFN membranes.

The HMSN-TFN membranes were fabricated according to the above-mentioned method except the incorporation of HMSN at different concentrations (0.01, 0.0325, 0.05 and 0.1 wt%). The HMSN were dispersed in the MPD solution before the interfacial polymerization process. To ensure the HMSN could be well dispersed, the mixture was sonicated for 1 h in an ultrasonication bath at 22 °C exactly before the interfacial polymerization process. For the ease of reference, TFN membranes are named according to their initial HMSN incorporation concentrations and the 0.0325 wt% concentration is noted as 0.03 wt% in this study.

2.4. Characterization of nanoparticles, TFC and TFN membranes

Malvern Zetasizer Nano ZS (Malvern Inst. Ltd., U.K.) was used to obtain the particle size distribution of PtBA and the surface charge of the HMSN based on the dynamic light scattering (DLS). The samples were prepared by the dispersion of the HMSN in the milli-Q water and the measurements were performed at room temperature.

A NICOLET 6700 attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) equipped with a diamond ATR was used to evaluate the chemical functionalities of the various fabricated nanoparticles and membranes.

Thermogravimetric analysis (TGA) was performed using a TGA/DSC 2 STAR^e System from 30 to 800 °C at a heating rate of 10 °C/min under air. An isotherm at 120 °C was set for 1 h during TGA analysis to remove the physically adsorbed water.

The structure of the HMSN and the surface and cross-section morphologies of the fabricated membranes were characterized using a scanning electron microscope (FEI Quanta 450 FEG Environmental SEM (ESEM)) with the voltage of 10 kV and the working distance of 10 mm. The microscope was equipped with an energy-dispersive X-ray (EDX) detector for elemental analysis. For