



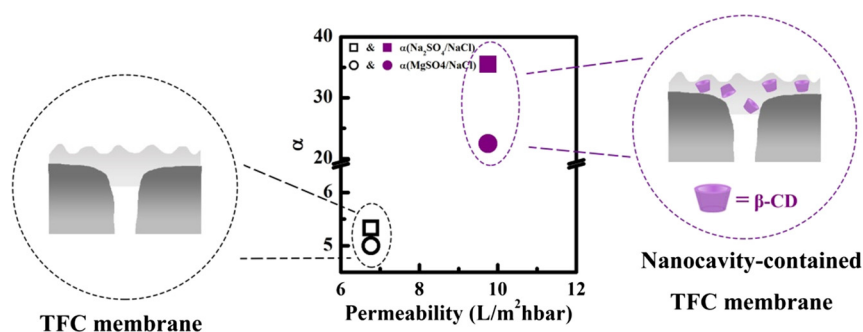
# Preparation of nanocavity-contained thin film composite nanofiltration membranes with enhanced permeability and divalent to monovalent ion selectivity

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Using hydroxypropyl-β-cyclodextrins (OH-β-CD) as aqueous phase additive, nanocavity-contained thin film composite (TFC) nanofiltration (NF) membranes were prepared by interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMC). Attenuated total reflectance Fourier transform infrared and X-ray photoelectron spectroscopy analysis confirmed the successful incorporation of OH-β-CDs into the thin polyamide rejection layers. The rejection layer morphologies and structures, surface properties and separation performances of the prepared TFC membranes were greatly influenced by the OH-β-CD mass ratio in aqueous phase during interfacial polymerization. With appropriate OH-β-CD mass ratios (20–60%), the prepared TFC membranes showed enhanced water flux, reduced  $R_{NaCl}$ , increased  $R_{Na_2SO_4}$  and  $R_{MgSO_4}$ , which led to highly improved divalent to monovalent ions selectivity. These nanocavity-contained TFC membranes exhibited the potential to apply in desalination pretreatment.

## 1. Introduction

Nanofiltration (NF) membranes, capable of removing most of divalent ions, multi-valent ions, natural organic matter and dyes, have been widely applied in desalination pretreatment, water softening and wastewater reclamation [1–4]. Ideal NF membranes shall have high

water permeability and high solute selectivity (e.g. divalent to monovalent ion selectivity) [4,5]. A common method to form nanofiltration membranes is through the interfacial polymerization of an acyl chloride monomer and an amine monomer [6–10]. This reaction forms a thin polyamide rejection layer that is often supported by a porous substrate, a structure known as thin film composite (TFC). The permeability and

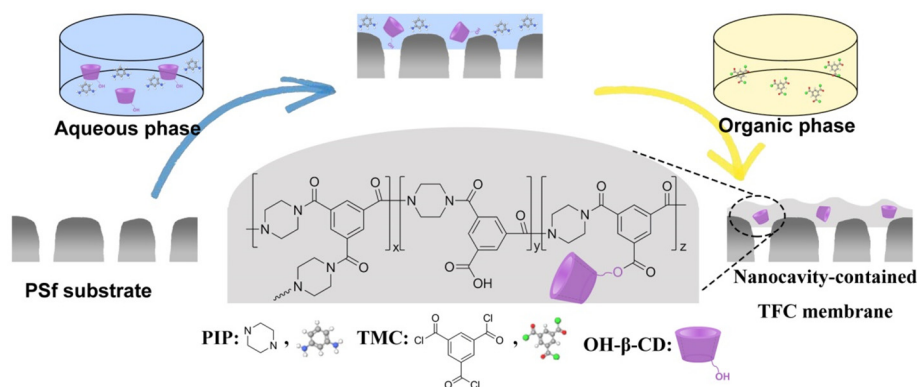
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Scheme 1. Diagram of the preparation process and the role of OH-β-CD in the interfacial polymerization.

selectivity of the resulting TFC membrane are strongly dependent on the morphology and structure of the thin polyamide rejection layer [10–14]. The latter in turn depends on the composition of aqueous and organic phases [6,10,15], the properties of substrate [16,17] and other reaction conditions such as temperature [9,18]. In a recent study [13], a nanofoaming method was developed to increase water permeability and salt rejection simultaneously by enhancing the formation of nanosized voids in the thin polyamide layer.

An alternative way to form nanofoamed TFC membranes is to incorporate nanocavities into the thin polyamide layer. β-Cyclodextrin (β-CD) is a cyclic oligosaccharide consisting of seven glucopyranose units linked by α-(1,4) bonds, with the doughnut-shaped molecular structure containing a hydrophobic nanocavity and hydrophilic exterior (Fig. S1) [19,20]. Based on this special structure, β-CD has been applied for gas purification [21,22], pervaporation [23–25], micropollutants adsorption [26–28] and membrane-based pressure-driven separation [29–33]. Only a few papers have reported the NF membranes with β-CDs contained rejection layer [29–31]. These NF membranes showed improved water permeability but moderate divalent ions rejections.

In this study, hydroxypropyl-β-cyclodextrins (OH-β-CD) were incorporated into the polyamide thin film by interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMC). Due to the hydroxyl groups in the side chain, hydroxypropyl modified β-CDs (OH-β-CDs) were used to improve the loading amount and their bonding to the polyamide matrix [33]. The diameter of the cavity of OH-β-CD molecule is just in the range between water molecules and most of salt ions (Fig. S1 and Table S1). Thus, with the addition of OH-β-CDs, the formed nanocavity-contained TFC membrane was proposed to show improved water permeability, whereas slightly changed divalent salts (e.g. Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>) permeability, simultaneously increased monovalent salts (e.g. NaCl) permeability due to the spaces between OH-β-CDs [31]. The morphologies, surface properties and separation properties of the nanocavity-contained TFC membranes were systematically investigated to understand and confirm the above proposition.

## 2. Experimental

### 2.1. Materials

Piperazine (PIP, 99%, Sigma-Aldrich) was used as the aqueous phase monomer in interfacial polymerization. Hydroxypropyl-β-cyclodextrin (OH-β-CD, 99%+, Adamas reagent CO., Ltd.) was used as the aqueous phase additive. N-hexane (for HPLC, ≥95%, Sigma-Aldrich) was used as organic phase solvent. Trimesoyl chloride (TMC, 1,3,5-benzenetricarbonyl trichloride, 98%, Sigma-Aldrich) was used as organic phase monomers. Polysulfone (PSf, Mw~35,000, Sigma-Aldrich) was used to prepare the porous substrates. Dimethylformamide (DMF, anhydrous 99.8%) was purchased from Sigma-Aldrich. Trisodium phosphate dodecahydrate (Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O, AR), sodium chloride (NaCl,

AR), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, anhydrous, AR), magnesium sulfate (MgSO<sub>4</sub>, anhydrous, AR), glucose (AR) and amantadine hydrochloride (98%, AR) were obtained from Dieckmann company. Deionized water used throughout this work was supplied from a Milli-Q system (Millipore).

### 2.2. Preparation of polysulfone porous substrate

The PSf porous substrate was prepared by the non-solvent induced phase separation method according to our previous work [34]. In summary, a 15 wt% PSf solution was prepared by dissolving PSf pellets in DMF. The solution was heated at 60 °C overnight for degassing. Then the solution was spread into a film on a glass plate by an automatic film applicator (Elcometer 4340, Elcometer, adjusted at a gate height of 150 μm). The nascent film was coagulated in a deionized water bath at room temperature (25 ± 1 °C.) and the formed substrate was stored in deionized water before further use.

### 2.3. Preparation of TFC membrane

In current study, a thin rejection layer was formed on the PSf porous substrate by interfacial polymerization following a reported procedure [16]. The preparation process was shown in Scheme 1. Briefly, PIP and OH-β-CD with different mass ratios were dissolved in deionized water and used as aqueous phase solution. The total concentration of the PIP and OH-β-CD was fixed at 1 wt%. An additional 0.6 wt% Na<sub>3</sub>PO<sub>4</sub> was added into the aqueous phase solution and used as acid acceptor. A 0.05 wt% TMC in n-hexane solution was used as the organic phase solution. To fabricate the TFC membranes, the PSf porous substrate was rinsed with deionized water and then immersed in the aqueous phase solution for 2 min. The residual droplets of aqueous solution were removed by a rubber roller. Afterwards, the organic phase solution was poured onto the substrate and the reaction was continued for 1 min. The resultant membrane was rinsed using n-hexane and immersed in deionized water at 50 °C for 10 min for further polymerization. Finally, the prepared membrane was stored in deionized water before characterization. The prepared TFC membranes were named as TFC<sub>n</sub>, where n referred to the mass ratio of OH-β-CD. For example, TFC<sub>50</sub> was the TFC membrane prepared by using the aqueous phase solution with OH-β-CD mass ratio of 50%.

### 2.4. Membrane characterization

Membrane surface and cross-section (fractured in liquid nitrogen) morphologies were imaged by a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi) after sputter-coated with a thin layer of gold (SCD 005, BAL-TEC). Attenuated total reflectance Fourier transform infrared (ATR/FTIR, Nicolet 6700, Thermo Fisher Scientific LLC, USA) spectroscopy equipped with an ATR accessory (ZnSe crystal,

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