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Highly porous carbon nanotube/polysulfone nanocomposite supports for high-flux polyamide reverse osmosis membranes

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ABSTRACT

Recent studies have emphasized that the surface properties of support layers in thin-film composite (TFC) membranes play a significant role in reverse osmosis (RO) performance. In this study, we used carbon nanotubes (CNTs) to tune the surface properties of microporous polysulfone membranes. The prepared CNT/PSf nanocomposite supports showed significantly improved surface porosity while maintaining both surface pore radius and hydrophobicity. Such surface characteristics resulted in the defect-free formation of a polyamide (PA) selective layer possessing a large surface area, which led to enhancement in the flux of PA-TFC membranes. PA-TFC membranes prepared with CNT/PSf nanocomposite supports showed improved water permeance up to 35% without losing salt rejection compared to the bare PA-TFC membranes. The results revealed that the surface porosity of the support is a dominant factor influencing the water permeance of TFC membranes rather than the pure water flux inside the support itself or the thickness of the PA layer. We also propose a direction for generating optimal supports through a comparison study between CNTs and hydrophilic pore formers as additives in the support material.

1. Introduction

Desalination has become indispensable for human beings due to a population explosion and restricted water resources [1–3]. Membrane-based desalination has been favored over conventional water purification technologies such as distillation and physicochemical treatments because it is energy-efficient, simple, continuous, and easy to scale up [1,4,5]. The most popular desalination technology is reverse osmosis (RO). RO is based on thin-film composite (TFC) membranes, which consist of an ultrathin polyamide (PA) layer and a porous support reinforced by a nonwoven fabric [3]. Although TFC membranes have dominated the desalination market in recent decades, high-flux TFC membranes are still necessary to further reduce the energy consumption in operation processes [6,7].

Most studies have merely focused on the manipulation of a PA layer to achieve high-flux TFC membranes [8–10]. This is because it is believed that the PA layer alone determines the water permeance and salt rejection of TFC membranes [11,12]. However, recent studies on the supports of TFC membranes have emphasized that the surface properties of supports also play a significant role in the overall mass transport through TFC membranes [13–18]. Theoretically, an optimal support requires a higher surface porosity in high-flux TFC membranes to decrease the effective diffusion path-length of penetrating molecules [13,16,18,19]. A few experimental results have shown that improving the surface porosity can be an efficient method to enhance the water flux of TFC membranes [13–15]. Meanwhile, one must consider that the pore structure and surface chemistry of the supports could impact the formation of the PA layer during interfacial polymerization. For example, hydrophobic supports with a smaller pore size are desirable to prevent the PA layer from penetrating into pores, which deteriorates both water flux and salt rejection [17,20].

In general, RO supports are prepared by non-solvent-induced phase separation (NIPS), usually using polysulfone (PSf) [17]. NIPS is a useful method to control the membrane morphologies and mechanical properties [21], but it is difficult to obtain highly porous surface morphologies using NIPS [22]. Thus, some dope solutions used in the NIPS process contain hydrophilic additives, also known as “pore formers” (e.g., polyethylene glycol (PEG) [23], polyvinylpyrrolidone (PVP) [24] and glycerol [25]), to increase the bulk porosity of the membranes. However, such conventionally used pore formers simultaneously increase the hydrophilicity of the membranes due to their intrinsic hydrophilicity, which is not desirable for RO supports [17].

Nanomaterials are emerging as promising additives in dope solutions because they can be easily used to tune the structure and

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physicochemical properties such as hydrophilicity, porosity, and mechanical stability of membranes prepared by NIPS [26]. Among the various nanomaterials, carbon nanotubes (CNT) have drawn significant attention in ultrafiltration (UF) [27], nanofiltration (NF) [28,29], and RO membranes [30,31] due to their exceptionally high aspect ratio, low density, impressive mechanical properties, and extraordinary transport behavior of water molecules [8,32,33]. Considering all of these issues, we incorporated oxidized CNT (o-CNT) into PSf supports to prepare highly porous CNT/PSf nanocomposite supports. The prepared CNT/PSf nanocomposite supports showed significantly improved surface porosity while retaining similar surface pore radius and hydrophobicity compared to pristine PSf supports. We investigated the RO performances of TFC membranes prepared with CNT/PSf nanocomposite supports and provided a direction for future work to achieve optimal supports using a comparison study.

2. Experimental

2.1. Materials

PSf (Udel P-3500, BP Amoco, M_w: 80 kg/mol) was used to fabricate the supports. Multi-walled CNTs (outer diameter: 6–9 nm, length: 5 µm), PVP (M_w: 10,000), and PEG (M_w: 12,000) were purchased from Sigma Aldrich (US). *m*-Phenylenediamine (MPD) and trimesoyl chloride (TMC), also purchased from Sigma Aldrich, were used for interfacial polymerization of the PA layer. n-Decane (99%, extra pure), n-hexane (95%, extra pure), and sodium chloride (NaCl, 99%, extra pure) were purchased from Daejung Chemicals (South Korea). N, N-Dimethylformamide (DMF, 99.8%, anhydrous) was used as a solvent for PSf and was purchased from Sigma Aldrich. Sulfuric acid (H_2SO_4, 98%) and nitric acid (HNO_3, 70%), purchased from Daejung Chemicals, were used to oxidize pristine CNTs (p-CNTs).

2.2. Oxidation of CNTs (o-CNTs)

p-CNTs (1g) were treated with 250 ml of an H_2SO_4/HNO_3 (3/1, v/v) mixture for 3 h at 50 °C. The acid solution containing the CNTs was washed with deionized water several times and subsequently centrifuged for 30 min at 8000 rpm. The supernatant and precipitate of the solution were separated, and the precipitated CNTs were collected and dried in a vacuum oven for 24 h at 60 °C.

2.3. Preparation of PSf and CNT/PSf supports

Both PSf and CNT/PSf supports were prepared using the NIPS method. First, 7.85 g of PSf was dissolved in 42.15 g of DMF and was stirred overnight at 100 °C. The dope solutions were degassed for 20 min and cast onto a polyester non-woven fabric using a 150-µm-thick doctor blade. The resulting films were then immediately immersed into a 30 °C water bath, and as-prepared PSf supports were washed and stored in tap water at 5 °C for at least 24 h before use. To prepare CNT/PSf nanocomposite supports, given amounts of o-CNTs were dispersed in DMF using a bath sonicator (Branson 3510 MT, Branson, US) for 1 h, and the same procedure described above was conducted. We also incorporated PEG and PVP into the dope solution for the comparison study. Note that the concentration and molecular weight of each polymeric additive were selected within a range commonly used in previous reports [17,24,34–36]. The compositions of the supports are summarized in Table 1.

2.4. Preparation of TFC membranes with PSf or CNT/PSf supports

For the RO experiments, PA layers were fabricated on as-prepared supports via interfacial polymerization between MPD and TMC. The PSf or CNT/PSf supports were soaked in a 2 wt% MPD aqueous solution for 2 min. The remaining MPD solution was removed, and excessive water droplets were wiped from the surface of the support using a rubber roller. A 0.1 wt%/vol% TMC in n-decane solution was immediately poured onto the support, and the reaction was continued for 1 min. After polymerization, the remaining TMC solution was removed by rinsing with excess n-hexane. The membranes were washed several times with deionized water and stored in a deionized water bath for 30 min before use. The prepared TFC membranes with different composition of supports are listed in Table 1.

Table 1
The compositions of as-prepared supports and TFC membranes.

TFC membranes	Supports	PSf (wt%)	DMF (wt%)	Additives (wt%)
TFC-0	PSf-0	15.7	84.3	–
TFC-0.01	PSf-0.01	15.7	84.3	o-CNT 0.01
TFC-0.05	PSf-0.05	15.7	84.3	o-CNT 0.05
TFC-0.1	PSf-0.1	15.7	84.3	o-CNT 0.1
TFC-0.5	PSf-0.5	15.7	84.3	o-CNT 0.5
TFC-1	PSf-1	15.7	84.3	o-CNT 1
TFC-PEG0.5	PSf-PEG0.5	15.7	83.8	PEG (12k) 0.5
TFC-PVP0.5	PSf-PVP0.5	15.7	83.8	PVP (10k) 0.5
TFC-PEG5	PSf-PEG5	15.7	79.3	PEG (12k) 5
TFC-PVP5	PSf-PVP5	15.7	79.3	PVP (10k) 5

Note: The concentrations of o-CNT are with respect to the weight of PSf. The concentrations of additives (PEG and PVP) are with respect to the weight of the solution.

2.5. Characterization of CNTs and membranes

Fourier transform infrared spectroscopy (FT-IR, Sens IR Technologies, Danbury, CT, USA) was used to analyze the functional groups in the CNTs and supports. The morphologies of the supports and TFC membranes were observed using a field-emission scanning electron microscope (FE-SEM, JSM-700F, JEOL, Tokyo, Japan). A contact angle analyzer (Phoenix 300, SEO, Suwon, South Korea) was used to measure the hydrophilicity of the supports using at least 8 water droplets. Characterization of surface roughness was performed using an atomic force microscope (AFM, XE-100, Park Systems, Sungnam, South Korea) over a 10 × 10-µm^2-sized area. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Co., US) was used to investigate the chemical composition of TFC membranes fabricated with different supports.

The surface pore radius and surface porosity of the supports were calculated using ImageJ 1.50i software (National Institute of Health, https://imagej.nih.gov/ij/). This characterization method has been widely used to determine the surface morphologies of supports [13,14,18,37]. At least three SEM images of each support from different areas were chosen to measure the surface pore radius and surface porosity, and the average values of each parameter are reported here.

Bulk porosities of supports were calculated using the following equation:

$$\text{Bulk porosity}(\%) = \frac{(w_{wet} - w_{dry})/\rho_{water}}{(w_{wet} - w_{dry})/\rho_{water} + w_{dry}/\rho_{polymer}} \times 100 \tag{1}$$

where w_{wet} is the weight of the wet support sample soaked in deionized water for 48 h, w_{dry} is the weight of the dried support sample stored in a vacuum oven for 24 h at 40 °C, ρ_{water} is the density of water (1 g/ml), and $\rho_{polymer}$ is the density of PSf [38].

The dispersibility of pristine CNTs and o-CNTs in DMF was evaluated using the following procedure [39]. First, 20 mg of each CNT was dispersed in 20 ml of DMF by bath-sonication for 1 h. After the dispersion process, each solution was left for one week, and a photo was taken to observe the dispersion state by overturning vials containing each solution. Quantitative dispersibility was also measured using the following method. Pristine CNTs and o-CNTs were dispersed in DMF (1g/L) and bath sonicated for 1 h. The solutions were left for one week and subsequently centrifuged for 30 min at 5000 rpm. The supernatant of each solution was filtered using weight-measured Anodisc