**Fabrication of Carbon Nanotube Membrane for Enhanced Performance in Forward Osmosis Process**

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**Abstract.** In this study, we investigated the effect of carbon nanotubes (CNTs) and performance of the prepared membranes. Thin film composite (TFC) forward osmosis (FO) membranes were fabricated based on the polyacrylonitrile (PAN) substrate, incorporating carbon nanotubes (CNTs) in the active skin layer. The CNTs can improve the water flux through added the hydrophilic groups. The mean surface roughness and hydrophilicity increased with the concentration of carbon nanotubes increased. The TFC membranes incorporated CNTs (0.2 wt%) exhibited the best FO performance with water flux of 25.14 L/m²·h and reverse salt flux of 8.64 g/m²·h using 0.5 M NaCl as draw solution and DI water as feed solution during FO test. The research provides us a promising approach to fabricate the high flux FO membranes.

**Introduction**

The forward osmosis (FO) process has attracted growing interest in the development of energy efficient, water treatment technologies since this process requires a very low hydraulic pressure, less energy input, and lower fouling tendency[1, 2]. As the most important components, the performance of FO membranes directly determines the treatment effect. It has been widely recognized that an ideal FO membrane fabricated through interfacial polymerization should have a thinner highly porous substrate to alleviating the internal concentration polarization (ICP) and achieving a high water flux, and a selective layer with high dissolved solute rejection[3]. In order to achieve the desirable properties, some of new concepts were introduced by various groups in the literature. Nanotechnology as a new way to improve membranes performance have rapidly growing interest[4].

Carbon nanotubes (CNTs) were paid attention by the unique properties exhibited such as its good biocompatibility, high mechanical strength, chemical stability and good thermal stability[5, 6]. It was reported that a high loading of CNTs likely resulted in a pore network in the membrane, and the hollow nanochannels of CNTs and their interspaces could provide new water transport channels[7]. More and more researchers used CNTs as modification to improve membrane performance. Wang[5] dispersed carboxylated CNTs in casting solution to fabricate support of thin film composition (TFC) FO membranes, which showed that the performance of the TFC membranes is better than the commercial one.

In this study, the effect of carbon nanotubes on the properties of TFC forward osmosis membranes was investigated. Various concentrations of CNTs were added into m-phenylenediamine (MPD) solution. And, the effects of different CNTs concentrations on the membrane permeability, surface morphology and structure were investigated.

**Materials and Methods**

**Materials**

Carbon nanotubes (CNTs, >95%, diameters of ~8nm, lengths of 0.5-2nm, 95%) is from Nanjing XFNANO Materials Tech Co., Ltd.; Polyacrylonitrile (PAN, Mw ~ 150000), m-phenylenediamine
(MPD, 99%), trimesoyl chloride (TMC, 98%), were obtained from Shanghai Sigma-Aldrich Co. Ltd.; 1-methyl-2-pyrrolidone (NMP, analytical grade), Sodium dodecyl sulphate (SDS), sodium chloride (NaCl, analytical grade) were purchased from Sinopharm Group Chemical Reagent Co., Ltd.; Polyethyleneimine (PEI, 30%) were purchased from Tisi Ai (Shanghai) Chemical Industry Co., Ltd.; Polyacrylic acid (PAA, Mw ~ 240000) were purchased from J&K Chemical Ltd. Technology; Isopar-G solvent (99.9%) was purchased from Mobil Oil; Deionized water (DI) was made in laboratory.

Membrane Preparation

14wt% of PAN was dissolved in NMP at 60 °C with stirring for 24 h. Then, the polymer solution after deaeration was casted on PET nonwoven fabric with a casting thickness of 100μm, followed by immersion in a coagulation bath. The prepared PAN support were thoroughly rinsed with DI water and then soaked into a 2.0 M NaOH solution for 1h to hydrolyze the support. The hydrolyzed PAN support was rinsed with 0.1 wt% PEI for 15 min, followed by immersed in deionized water for 5min, then placed in 0.1wt% PAA for 10min and deionized water for 5 min. The PAN-PEI/PAA support layer was prepared. Next, the polyamide selective layer was formed on the hydrolyzed PAN support by the reaction of aqueous solution and organic solution. To investigate the effect of CNTs on the performance of TFC membrane, three concentrations of CNTs (0.1wt%, 0.2wt%, 0.3wt%) were added into aqueous solution contained 2 wt% MPD. The organic solution was formed by dissolving TMC (0.15 wt%) into the Isopar-G solution. The polyamide active layer was formed through IP. Firstly, the PAN support was soaked into MPD solution for 2 min. Then the excess MPD solution was removed, and the substrate surface was blown dry again. Afterwards, the absorbed MPD support was homogeneously contacted with a 0.15 wt% TMC solution in Isopar-G for 1 min. Repeated the step again and then dried in the oven at 80°C for 10min. Finally, the resultant membranes were rinsed completely and stored in plastic box with DI water prior to use.

Characterization of TFC Membranes

The membrane morphology was observed using a field emission scanning electron microscopy (SEM, S-4800, HITACH). The surface roughness was studied by atomic force microscopy (AFM, Dimension3100, VEECO). The hydrophilicity of the TFC membrane was conducted using a contact angle meter (CA, OCA15EC, Data physics). The chemical structure of the membrane was analyzed by Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet 6700, Thermo Fisher). All the TFC membranes used for analysis were freeze-dried and placed in a dry sample bag to store.

Evaluation of FO performance

FO performance of the fabricated TFC membrane was evaluated with home-made FO system[8]. The flow rate was kept at 10 cm/s. DI water was used as the feed solution (FS), 0.5 M NaCl solution was used as the draw solution (DS). FO performance was measured in FO mode. FO water flux ($J_w$, L m⁻²h⁻¹=LMH) was determined by measuring the volume change of the FS($\Delta v$) for the effective membrane area (Am) and the given time interval ($\Delta t$) as follows:

$$J_w = \frac{\Delta v}{A_m \Delta t} \quad (1)$$

Reverse salt flux ($J_s$, g m⁻²h⁻¹=gMH) was determined by measuring the change of the salt concentration (C) and volume (V) for the given time interval as given by:

$$J_s = \frac{\Delta CV}{A_m \Delta t} \quad (2)$$

Results and Discussion

Figure 1 represents the SEM images of the surfaces for various TFC membranes. It can be observed that membrane surface is smooth at the absence of CNTs in the MPD solution (Figure 1a) and leaf-like structure on the surface[9]. With the concentrations of CNTs increased (Figure 1b-d), floccule appear on the membrane surface and gradually grow large, which is ascribed to CNTs.
agglomerate[10]. As shown in Figure 2, AFM images of active layers are obtained. The surface roughness also increases with the increase of CNTs concentration increased. It is worthy to note that the higher roughness, the larger surface area is available for membrane transport, which favors the improvement of the membrane flux[11].

![Figure 1. SEM images of morphologies of active layers formed under different CNTs concentration.](image)

Figure 2. AFM images of roughness of active layers under different CNTs concentration.

Figure 3 display the effect of CNTs concentration on the chemical structure of the composite membrane. The absorption peaks at 1540 cm\(^{-1}\) and 1662 cm\(^{-1}\) correspond to the groups of \(-\text{N}–\text{H}\) (amide II peak) and \(-\text{C}=\text{O}\) (amide I peak), respectively. The aromatic ring breathing of the PA layer is indicated by an absorption peak at 1611 cm\(^{-1}\). The stretching mode of \(\text{C}–\text{C}–\text{O}\) appear at 1034 cm\(^{-1}\), which could be explained by the introduction of carboxyl groups during the purification stage of the commercial CNTs production[12]. 1725 cm\(^{-1}\) is the absorption peak of \(\text{C}=\text{O}\) for carboxyl groups of CNTs, while the absorption peak appearing at 3000~3800 cm\(^{-1}\) is caused by the \(-\text{OH}\) group stretching vibration.

![Figure 3. ATR-FTIR spectra of active layers formed under different CNTs concentration.](image)

In order to analysis the hydrophilicity of TFC membranes, the contact angles of TFC membranes were tested (shown in Figure 4). The smaller the contact angle, the better the hydrophilicity of the membranes. The contact angles are decreased from 67.6° to 61.5° with the concentration of CNTs increase from 0 wt% to 0.3 wt%. It is possible that the carbon nanotubes contain hydrophilic groups
(carboxyl group and hydroxyl group) and improve the hydrophilicity of the membrane. The results confirm that CNTs could increase the surface hydrophilicity of TFC membrane.

![Figure 4](image.png)

Figure 4. Effect of different CNTs concentration on surface contact angle of thin-film composite membranes.

To test membrane permeation of TFC membranes, water flux and reverse salt flux were tested in FO mode (active layer facing feed solution, AL-FS). The results are shown in Figure 5. Water flux increase from 16.97 LMH to 32.31 LMH (0.3 wt%). The reason is probably that carbon nanotubes could provide channels for water molecules, as well as increase the hydrophilicity of the active layer [13]. While with the increase of the CNTs concentration, the reverse salt flux gradually increase from 6.02 gMH to 14.39 gMH.

Js/Jw is directly related to the membrane selectivity and determined by the intrinsic membrane transport parameter, as is shown in Figure 5(b). With the increase of the CNTs concentration, Js/Jw values are 0.35 g/L, 0.32 g/L, 0.37 g/L, 0.44g/L. It is found that the separation performance of the TFC membrane decrease firstly and then increase. Comprehensively, carbon nanotubes can improve the water flux obviously. When the CNTs concentration is 0.2 wt%, the water flux is about 25.14 LMH, the reverse salt flux is 8.64 gMH, the Js/Jw value is 0.37g/L, the membrane performance is relatively well.

![Figure 5](image.png)

Figure 5. Effect of different CNTs concentrations on water flux (a) and reverse salt flux (b) of various TFC membranes.

**Conclusion**

The effect of CNTs concentration on performance of TFC FO membranes was investigated. Based on this work, the following conclusions were summarized as following.

1. With the concentration of CNTs increase, the roughness and hydrophilicity of the surface
of TFC membranes increased. Floccule appeared on the active layer of TFC membranes in the presence of CNTs, which is probably due to CNTs particles agglomerate;

2. The performances of the TFC membranes in terms of water flux and reverse salt flux tested in FO process increased with the increase of CNTs concentration. The FO performance of the TFC membrane under the 0.2 wt% CNTs show the best performance with water flux of 25.14 LMH, reverse salt flux of 8.64 gMH, Js/Jw value of 0.37 g/L.

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References