

Preparation of Nano-silica Dioxide Modified Cellulose Acetate (CA) Membranes for Enhanced Performance in Forward Osmosis Process

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Abstract: Nano-silica dioxide (nano-SiO₂) modified cellulose acetate (CA) membranes for forward osmosis (FO) were prepared by phase inversion via immersion precipitation technique. Nano-SiO₂ particles were added into the casting solution of CA, 1, 4-dioxane, acetone, lactic acid and methanol to improve the FO membranes performance. Different percentage of nano-SiO₂ (2, 4 and 6 wt. %) of CA composite membranes were cast. The modified membranes were characterized by various methods to probe the membranes structure and surface properties. The FO performances were also evaluated for the modified membranes compared to the non nano-SiO₂ membranes. The surface hydrophilicity, porosity and tensile strength of nano-SiO₂ CA membranes were improved with the increment of the percentage of nano-SiO₂ added to the CA. The morphological studies showed that the addition of nano-SiO₂ significantly changed the surface properties of the CA membranes. The FO performance was evaluated using 1M NaCl solution as feed solution and purified water as draw solution. The nano-SiO₂ CA membranes showed better water flux and reverse salt flux in the range of 2–6 wt. % nano-SiO₂ content than original CA membranes. These encouraging results suggested that nano-SiO₂ CA membranes displayed potential to be further developed for FO applications.

1 INTRODUCTION

Forward Osmosis (FO) is the transportation of water across a selectively permeable membrane from a region with higher water chemical potential to a region with lower water chemical potential. This process is driven by a difference in solute concentrations across the membrane which allows passage of water but rejects most solute molecules or ions. Due to its inherent advantages, such as low energy expenditure, low membrane fouling, high water recovery, simple configuration and equipment and etc, forward osmosis process was extensively studied by scientists for a variety of applications in science and engineering (Cath et al., 2006; Shuaifei et al., 2012). Now, its applications have showed potential values in seawater desalination, wastewater treatment, food and pharmaceuticals

processing, controlling drug release, and electrical power generation (Shuaifei et al., 2012; Achilli et al., 2009), etc.

However, there are some problems which limit the use of FO, such as flux decline caused by internal concentration polarization, lack of proper draw solute and effective recovery. Recent works have focused on reducing internal concentration polarization and seeking optimal draw solute. The internal concentration polarization which occurs within the support layer is the major limiting factor causing the decline of water flux (McCutcheon and Elimelech, 2006). The influence of internal concentration polarization on FO water flux has been investigated by different modeling techniques and the solution-diffusion theory (Shuaifei et al., 2012). A variety of draw solutes/solutions, including magnetic and/or hydrophilic nanoparticles

and organic compounds (Kim et al., 2012; McCutcheon et al., 2005), have been investigated in FO process.

In the early study, reverse osmosis (RO) membranes were tested for FO process. But they showed low water flux due to the internal concentration polarization caused by the porous support layer. Hence, a perfect FO membrane should consist of a single active layer without any support layer (Wang et al., 2010). However, the lack of mechanical strength may limit its applicability. Chung's group developed flat-sheet CA-based membranes comprised double-skinned layers that were able to eliminate internal concentration polarization (Zhang et al., 2010; PhuongNgaNguyen et al., 2013). However, the membranes showed low water flux due to the additional resistance to water transport. Thi Phuong Nga Nguyen et al. prepared CTA/CA FO membranes to improve water flux (Smitha et al., 2004), but relatively high reverse solute flux (RSF) limits the application of the membranes. It is necessary to prepare FO membranes with high water flux and salt rejection for practical application.

Introducing inorganic particles into membrane materials has shown potential to improve the permeability and selectivity of membrane (Sairam et al., 2011). Nano-silica dioxide (nano-SiO₂) is one of the most important new high-tech ultra-fine inorganic materials and has lots of particular characteristics: the particle size of 20±5 nm, the high specific surface area of 640-700m²/g and superior thermal and chemical stability. Besides, the rich hydroxyl groups on the surface of nano-SiO₂ can form hydrogen bonds with the hydroxyl groups of polymer chains. In a word, nano-SiO₂ plays an irreplaceable role in many subjects due to its particular characteristics (Liu et al., 2004)].

In this research, nano-SiO₂ are added into the CA casting solution of 1,4-dioxane and acetone with additives of lactic acid and methanol to prepare the new nano-SiO₂ modified cellulose acetate (CA) membranes for FO application. Membranes are prepared by phase inversion. Subsequently, the new nano-SiO₂ modified CA membranes are characterized in different ways and compared with CA membranes without nano-SiO₂. The influences of the content of nano-SiO₂ on the membrane performance are also discussed.

2 MATERIAL AND METHODS

2.1 Materials

CA(54.5 ~ 56.0wt. % acetyl) were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. 1, 4-dioxane (≥99.5%purity), acetone (≥99% purity), lactic acid (≥99%purity) and methanol (≥99.8% purity) were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium chloride (NaCl, 99%purity) and deionized water were used for membrane performance testing. Nano-silica dioxide (7nm) was from Sinopharm Chemical Reagent Co., Ltd and used for modifying. Disodium carbonate (Na₂CO₃, Sinopharm Chemical Reagent Co., Ltd) was used as an effluent for ion chromatography (ICS-900, Dionex, CA, USA).

2.2 Preparation of Flat-sheet CA-based Membrane and Nano-SiO₂ Modified CA Membrane

Flat-sheet membranes were prepared by phase inversion. The casting solution contained CA polymers dissolved into 1, 4-dioxane and acetone with additives of lactic acid and methanol (Sairam et al., 2011). The solution was kept in a round flask sealed with a glass stopper to prevent evaporation of the solvents. The solution was homogenized by using a mechanical stirrer (JJ, Yitong Electron Co., Ltd, China). The casting solution was then cast on a glass plate by using a 100mm thick casting knife in a constant temperature (set up at 25°C) and humidity (70% relative humidity) room. After evaporation of the solvent for 30s, the casting film together with the glass plate was immersed in a coagulation bath of 1±0.3°C deionized water. The membrane was then stripped off the glass plate and kept in a bath of deionized water at room-temperature (20°C), which was changed every 4h for 24h to wash out the solvents. Then the membrane was stored in deionized water for performance testing.

The compositions of casting solution were of 13.4 wt. % CA, 53.2 wt. % 1, 4-dioxane, 18.4 wt. % acetone, 6.8 wt. % lactic acid and 8.2 wt. % methanol. The nano-SiO₂ were added into the solution in different contents (2, 4 and 6 wt. %) and were dispersed by stirring for 8h at room temperature. The resultant solution was prepared for phase inversion after eliminating air bladder by

sonic oscillating. The nano-SiO₂ modified CA membranes are denoted as CAN-2, CAN-4 and CAN-6 assigned to their nano-SiO₂ content.

2.3 Characterization of Membrane Structure and Surface Properties

Scanning electron microscopy (SEM) was used to acquire the cross section and top surface imaging of membranes to determine the morphological properties. The SEM analysis was performed using FEI Quanta 200 from Holland and operated at 15 KV. Every membrane sample was dried under vacuum for 24h to dehydrate it for preparing SEM samples. Membranes were fractured in liquid nitrogen to clearly scan the cross-section image. The membranes were coated with a gold layer for observation by a sputter coater. Furthermore, energy dispersive spectrometer (EDS) was used to collect the elemental composition of membranes.

Attenuated total reflectance spectroscopy (ATR-FTIR) was used to analyze the chemical changes of the membranes in this study. Nicolet AVATAR 360 FTIR Spectrophotometer together with an ATR accessory (ZnSe crystal) was used to collect the spectra. The incidence angle was 45° and each spectrum was recorded using 32 scans at a resolution of 4cm⁻¹ in the region between 400 and 4000 cm⁻¹. OMNIC 8.2 software was used to record the spectra, correct their baselines, normalize the spectra and find the peaks.

Contact angle measurements were conducted by dynamic contact angle instrument (DSA100, KRÜSS GmbH, Hamburg, Germany). Contact angle indicates the hydrophilicity and the smaller angle indicates the better hydrophilicity. Every membrane sample was dried under vacuum for 24h before measurement. Two replicates were used, and five drops per replicate were measured.

Membranes porosity(ϵ) was calculated from the equations below (Wang et al., 2010):

$$\epsilon = \frac{(m_{\text{wet}} - m_{\text{dry}})/\rho_w}{(m_{\text{wet}} - m_{\text{dry}})/\rho_w + (m_{\text{dry}}/\rho_p)} \times 100 \quad (1)$$

Where m_{wet} and m_{dry} are the mass of the hydrated and dried samples, ρ_w and ρ_p are the density of water and polymers at a dried state respectively. The relative density of the CA polymers used is 1.31 g/cm³ according to the reagent instructions.

Mechanical properties (e.g., tensile strength) of the CA membranes and modified nano-SiO₂ CA

membranes were measured using a universal tensile testing machine (AGS-J, Shimazu, Japan). Every membrane sample was dried under vacuum for 24h before measurement. The elongation velocity was 2 mm/min with an initial gauge length of 15 mm.

2.4 Performance Testing

The prepared membranes were tested in FO mode using a test cell with 30.25cm² effective area (width, 6.5 cm; length, 6.5 cm). Either feed solution or draw solution was kept in a 2L tank. Both solutions were circulated at a rate of 15 L·h⁻¹ in a closed loop by using two diaphragm pumps (PLD-2203, China). The draw solution was placed on a weighing balance and the feed solution was placed on a platform at the same height to eliminate any gravitational effects. Feed solution was Purified water from a Milli-Q system(18M Ω cm) and draw solution was 1M sodium chloride (NaCl). Both of the volume of the solutions was 1L. Membrane performances were assessed by measuring permeate water flux (J_w) and reverse salt flux (J_s).

The permeate water flux (J_w) was calculated through the increment of the weight of the draw solution because of the water permeated over the membrane during the FO testing. The change of the weight was obtained by the weighting balance which the draw solution was placed on. Corresponding, the feed solution was put on a platform at the same height to eliminate any gravitational effects. The calculation equation of water flux was as follows.

$$J_w = \frac{\Delta w}{\rho \times A_m \times \Delta t} \quad (l/m^2 \cdot h \text{ or LMH}) \quad (2)$$

Where Δw is the change of the weight of the draw solution, ρ is the water density, A_m is the effective membrane area and Δt is the time of testing.

RSF (reverse salt flux) was defined as the mass of NaCl diffusing from the draw solution to the feed solution per unit time per unit membrane area during FO testing. The mass of NaCl was obtained through the concentration of chloride ions in each solution which was determined by ion chromatography. 10 mL samples of both solutions were collected for determination before and after the testing. The calculation equation of RSF was as follows:

$$J_{s-\text{NaCl}} = \frac{w}{A_m \times \Delta t} \quad (\text{g}/\text{m}^2 \cdot \text{h}) \quad (3)$$

Where w is the mass of NaCl, A_m is the effective membrane area and Δt is the time of testing.

The membrane performances were tested in AL-FS (active layer facing feed solution) orientation. Data were recorded after running of the system for 5 min to stabilize water flux and the testing time was 1 h. All the tests were conducted at 25°C and repeated three times to minimize experimental error.

3 RESULTS AND DISCUSSIONS

3.1 FO Membrane Morphologies

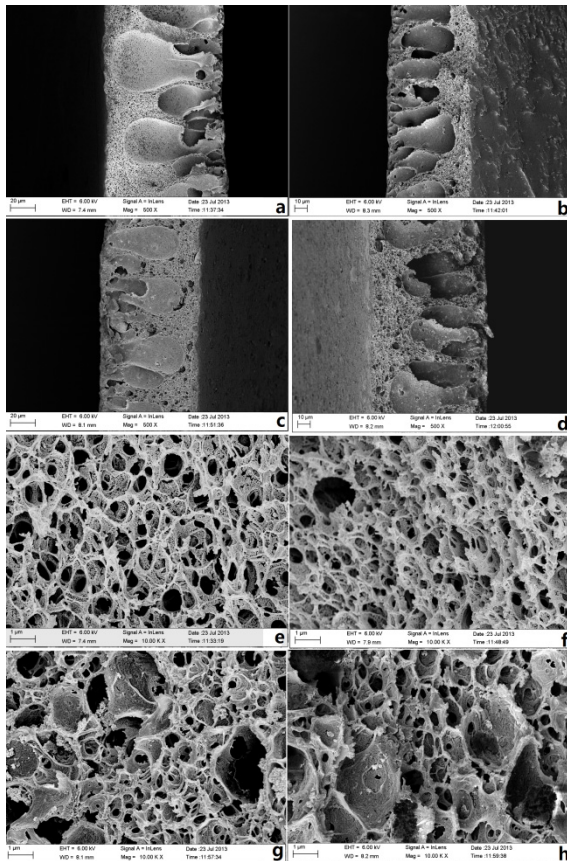


Figure 1: SEM cross sectional micrographs of CA membranes prepared with: (a) 0 wt. % nano-SiO₂, (b) 2 wt. % nano-SiO₂, (c) 4 wt. % nano-SiO₂ and (d) 6 wt. % nano-SiO₂ and amplified SEM cross sectional micrographs of CA membranes prepared with: (e) 0 wt. % nano-SiO₂, (f) 2 wt. % nano-SiO₂, (g) 4 wt. % nano-SiO₂ and (h) 6 wt. % nano-SiO₂.

In the text, Figure 1 (a) to Figure 1 (d) shows the cross-section morphology of CA membranes prepared with different content of nano-SiO₂ in the casting solution. The SEM images indicated that the asymmetric structure of the membranes was not changed by the presence of nano-SiO₂. All the membranes show the asymmetric structure of compact cortical layer and porous support layer containing the finger-like structures. The Figure 1 (e) to Figure 1 (h) shows the amplified images of the finger-like structure of the membranes and show that the large pores appear gradually on the surface of the support layer increase with the increment of the content of nano-SiO₂. The reason is that the addition of nano-SiO₂ delays the process of the phase separation during the preparation of membranes, which plays an important effect on the membrane structure.

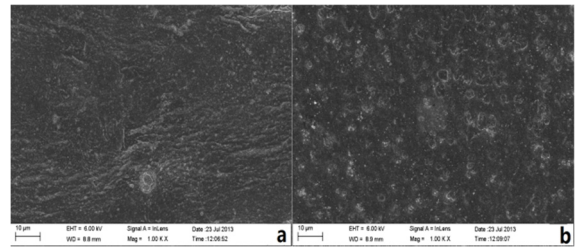


Figure 2: SEM micrographs displaying the top surfaces of CA membranes prepared with: (a) 0 wt. % nano-SiO₂ and (b) 2 wt. % nano-SiO₂.

Figure 2 shows the surface morphologies of CA membrane (a) and modified CA membranes prepared with 6wt. % nano-SiO₂ in the casting solution (b). The particles can be clearly seen on the surface of the membrane when the nano-SiO₂ are added in the casting solution.

Table 1: Contact angle, porosity and mechanical strength of prepared FO membranes.

Membrane	Contact angle (°)	Porosity (%)	Tensile strength (MPa)
CA	67.1±0.72	47.52	6.17
CAN-2	54.1±0.83	52.20	7.79
CAN-4	49.3±0.21	57.57	8.63
CAN-6	43.6±0.54	61.64	9.22

Table 1 indicates the surface contact angles, porosity and tensile strength of CA membranes prepared with different content of nano-SiO₂ (0, 2, 4 and 6 wt. %). The contact angle of membranes

declined with the increase of the content of nano-SiO₂, suggesting that the hydrophilicity of CA membrane surface was improved with the increment of the content of nano-SiO₂. This is due to the silicon hydroxyl groups on the membrane structure by the presence of nano-SiO₂ in the CA polymer system. Meanwhile, the porosity of membranes increased with the increase of the content of nano-SiO₂. This is because pores were formed when the nano-SiO₂ added in the casting solution filtered out of the main body of the membrane during the phase inversion (Lin et al., 2012). The tensile strength of the membranes was also improved with the increase of the content of nano-SiO₂.

3.2 ATR-FTIR Spectra and EDS of CA and Nano-SiO₂ Modified CA Membranes

Figure 3 shows the ATR FT-IR spectra of the CA membranes prepared with different content of nano-SiO₂ (0, 2, 4 and 6 wt. %). The appearance of peaks at 1739 cm⁻¹ corresponds to the carbonyl (C=O) of CA. The appearance of peaks at 1040 cm⁻¹ and 1228 cm⁻¹ is assigned to the ether group (C-O-C) of CA. The appearance of peaks at 3466 cm⁻¹ corresponds to the hydroxyl (-OH). There are no characteristic peaks in relation to silica oxygen group (Si-O-Si) and silicon carbon group (Si-O-C). It is also suggested that there is no silicon hydroxyl group (Si-OH) since the intensity of the peak of hydroxyl (-OH) is weak.

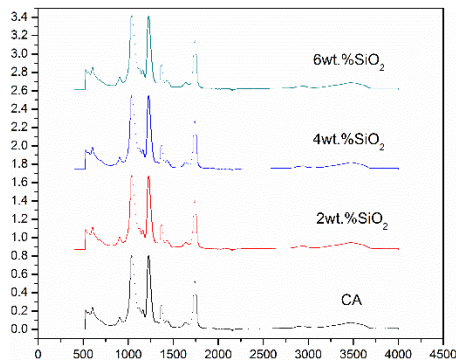


Figure 3: ATR FT-IR spectra of the CA membranes prepared with different content of nano-SiO₂ (0, 2, 4 and 6 wt. %).

Figure 4 shows the EDS of the CA membranes prepared with different content of nano-SiO₂ (0, 2, 4 and 6 wt. %). It clearly demonstrates that silicon element exists in the

membrane after modification by nano-SiO₂. In addition, the intensity of the peak of silicon in the EDS increases with the increase of the content of nano-SiO₂. With the FT-IR results, it can be concluded that nano-SiO₂ did not react with CA to form a new chemical bond. The addition of nano-SiO₂ plays a role of physical blending and nano-SiO₂ consists in the CA organic system as an additive.

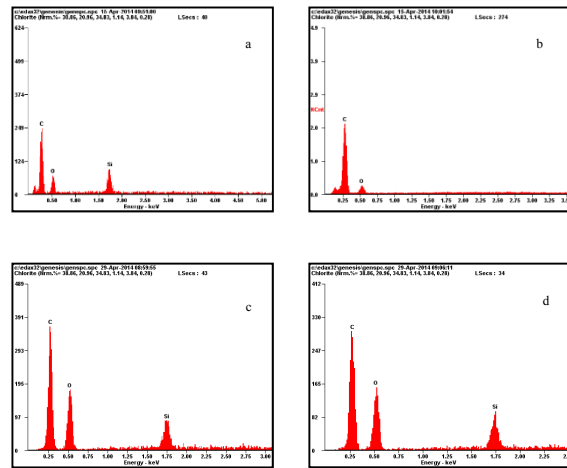


Figure 4: EDS of the CA membranes prepared with different content of nano-SiO₂ (0, 2, 4 and 6 wt. %).

3.3 Determination of FO Performance

Figure 5 shows the FO performance of CA membranes prepared with different content of nano-SiO₂ (0, 2, 4 and 6 wt. %) including water flux, reverse salt flux and salt rejection and the detailed data is listed in Table 2. It is worthwhile to note that the nano-SiO₂ modified CA membranes for FO exhibits superior separation properties than unmodified CA membrane. The water permeability and salt rejection were improved with the increase of the content of nano-SiO₂ in the CA membrane structure in the range of 0–4 wt. %. When the content of nano-SiO₂ increased from 0 wt. % to 4 wt. %, the water flux was improved from 6.15 LMH to 16.62 LMH and the reverse salt flux declined from 9.67 to 3.85 g NaCl/m² h. The improvement in water flux of nano-SiO₂ modified CA membranes could be attributed to the existence of nano-SiO₂ that forms nanochannels in the top surface of the membranes. Both inner cores of nanotubes (internal nanochannels) and the interfacial gap between nano-SiO₂ and CA polymer at the interface of CA layer (external nanochannels) create additional passage for solvent transfer. The latter plays a dominant role

since the internal nanochannels are too thin to extract water without applying pressure (FO mode). Moreover, the external nanochannels create direct and appropriate path in comparison with the inner cores (Ma et al., 2012). Also, the presence of nano-SiO₂ increases the surface hydrophilicity of FO membranes, which causes improvement of the water permeation through the modified FO membranes. The higher salt rejection is caused by the improvement in surface hydrophilicity, which promotes the water preferential adsorbing and decreases reverse salt flux. Reverse salt flux is proportional to the salt rejection coefficient R (Cath et al., 2006) and the lower reverse salt flux represents the higher salt rejection (Ng et al., 2006). It is worthwhile to note that both of the water flux and reverse salt flux of the modified membrane decrease when the content of nano-SiO₂ further increases from 4 wt. % to 6 wt. %, which might be attributed to the defect of nano-SiO₂ agglomeration in the phase inversion process. Hence, the excessive addition of nano-SiO₂ may not be advisable for FO applications. In summary, these results specified that the nano-SiO₂ modified CA membranes exhibit improved salt rejection as well as water permeability than unmodified membrane in FO process.

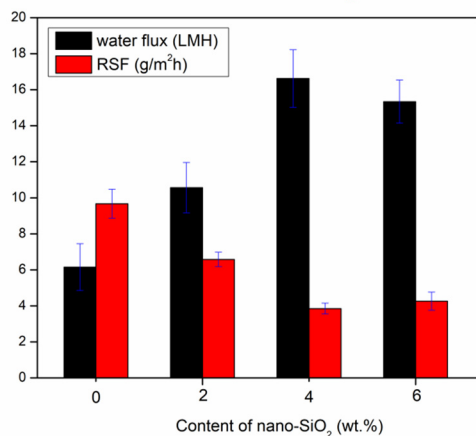


Figure 5: Water flux and reverse salt flux of the CA membranes prepared with different content of nano-SiO₂.

4 CONCLUSIONS

Nano silica dioxide (nano-SiO₂) modified cellulose acetate (CA) membranes were prepared. The FO performance of the modified membranes were evaluated and compared with those membranes

without nano-SiO₂. The addition of nano-SiO₂ does not change the asymmetric structure of CA membrane. The hydrophilicity, porosity and tensile strength of the membranes were improved with the increase of the content of nano-SiO₂ in the CA polymer system. The nano-SiO₂ did not react with the CA but consisted in the CA organic system as an additive according to the FTIR results. The smart selection of the nano-SiO₂ in order to use in FO membranes structure caused the formation of membranes with sufficient separation properties and FO performance. The water flux and salt rejection were simultaneously improved in the nano-SiO₂ modified CA FO membranes. However, excessive addition of nano-SiO₂ might decreased the permeability and selectivity of the membranes. Finally, it can be concluded that nano-SiO₂ modified CA membranes have potential for practical FO application as a result of their enhanced structural and separation properties.

Table 2: Water flux and reverse salt flux of prepared FO membranes.

membrane	Water flux J_w (LMH)	Reverse salt flux J_s -NaCl (g NaCl/m ² h)
CA	6.15	9.67
CAN-2	10.56	6.58
CAN-4	16.62	3.85
CAN-6	15.34	4.26

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