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Cellulose Nanocrystal-assembled Reverse Osmosis Membranes with High Rejection Performance and Excellent Antifouling

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SUPPLEMENTARY INFORMATION

S1. Performance optimization of the CNC-TFC membrane

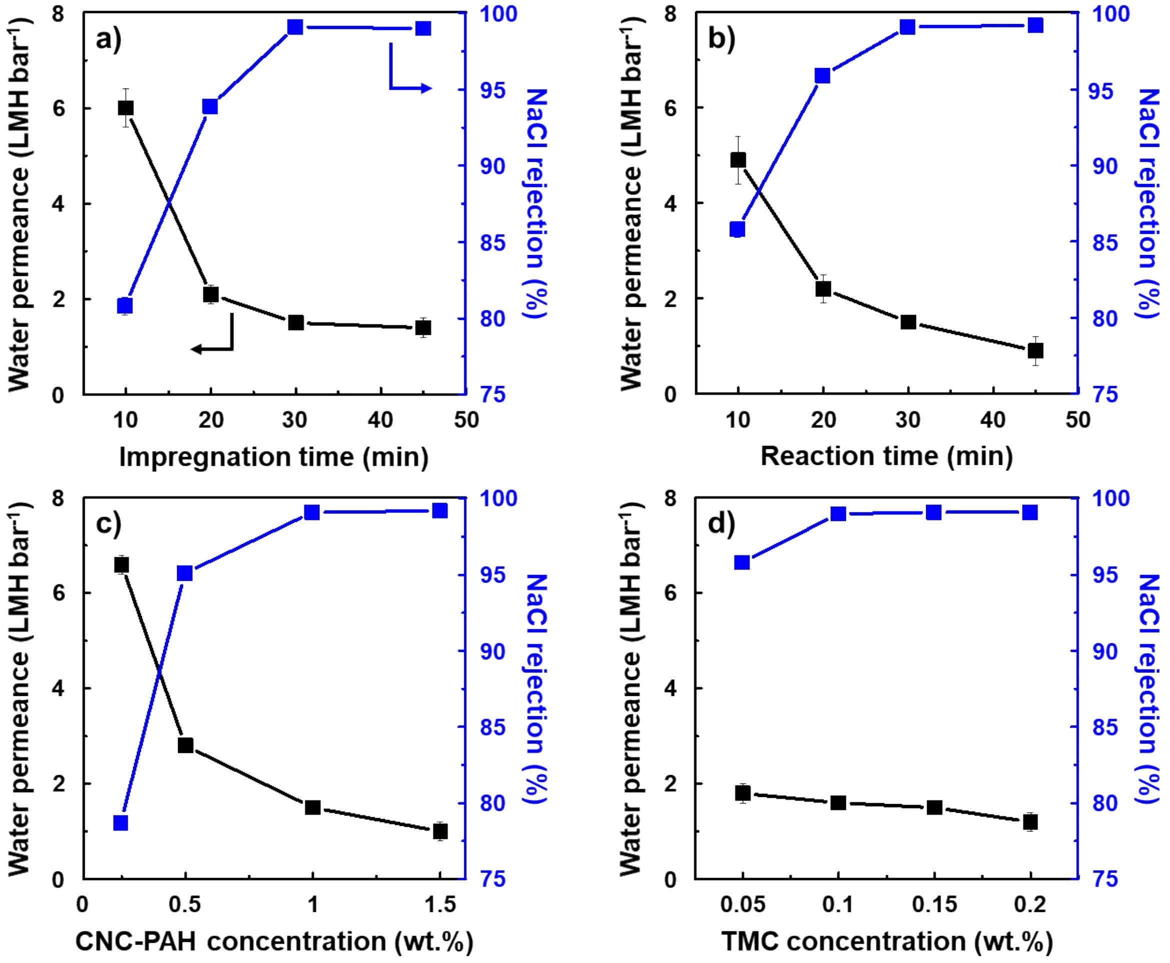

Fig. S1. Separation performance of the membranes (CNC-TFC) prepared using CNC-PAH as a function of (a) the impregnation time (reaction time = 30 min, CNC-PAH concentration = 1 wt.%, TMC concentration = 0.15 wt.%), (b) the reaction time (impregnation time = 30 min, CNC-PAH concentration = 1 wt.%, TMC concentration = 0.15 wt.%), (c) the CNC-PAH concentrations (impregnation time = 30 min, reaction time = 30 min, TMC concentration = 0.15 wt.%) and (d) the TMC concentrations (impregnation time = 30 min, reaction time = 30 min, CNC-PAH concentration = 1 wt.%). The process parameters for achieving NaCl rejection above 99% with the highest water flux were selected as the optimum conditions.

S2. Characterization of natural seawater

Table S1. The quality of natural seawater.

	pH	Conductivity (mS)	Turbidity (NTU)	TDS (g L^{-1})	TOC (mg L^{-1})
Raw water	7.4 ± 0.1	40.4 ± 0.5	1.48 ± 0.3	49.2 ± 0.8	23.8 ± 1.1
Pretreated water	7.5 ± 0.1	39.2 ± 0.6	0.91 ± 0.2	47.5 ± 0.6	18.7 ± 0.3

Collected natural seawater was pretreated with a microfiltration filter (0.45 µm pore size) to remove large foulants. Raw and pretreated seawater was characterized using various analyzing methods: A pH meter (Orion Star A221, Thermo Fisher Scientific, Waltham, MA) and a turbidity meter (Hach 2100P, Hach Company, Loveland, CO) were used to measure pH and turbidity, respectively. An Ultrameter II (Myron L Company, Carlsbad, CA) was also used to determine the conductivity and total dissolved solids (TDS). A total organic carbon (TOC) analyzer (Sievers 900, GE Analytical Instruments, Boulder, CO) was used to measure the organic concentration of water.

S3. Determination of the conversion rate of the hydroxyl groups on the CNC surface into initiators.

First, the amount of the initiators attached on the initiator-modified CNC (CNC-Br) surface was determined by hydrolyzing the ester group of the initiator and back-titrating with HCl.[1] CNC-Br (0.1 g) and an NaOH (0.5 N) solution (40 mL) were mixed in a round flask, and the mixture was heated to 60 °C for 15 min. Subsequently, the mixture was stirred at room temperature for 48 h. The amount of excess NaOH was back-titrated with 0.2 N HCl using phenolphthalein as an indicator. The amount of the ester groups was calculated using the following equation:

$$Ester\ group\ (mmol)\ per\ g = \left[(V_B - V_S) \times N_{HCl}\right]/W \qquad \text{(S1)}$$

where V_B is the volume of HCl required for blank titration, V_S is the volume of HCl required for titrating the sample, N_{HCl} is the normality of the HCl solution and W is the mass of the sample. The amount of the initiators attached to the CNC-Br surface was calculated to be 1.77 mmol g^{-1}.

In order to determine the conversion of the hydroxyl groups on the CNC surface into the initiators, it is necessary to know the total amount of the hydroxyl groups on the CNC surface. To quantify the amount of the surface hydroxyl groups of CNC, the hydroxyl groups were converted into the acetyl groups through acetylation, and the amount of the substituted acetyl groups was quantified by hydrolyzing the ester groups, followed by back-titration with HCl. The iodine (I_2)-catalyzed acetylation of CNC was used for high modification rate.[2] CNC (0.1 g) was dispersed in acetic anhydride (5 mL) with N_2 gas. The mixture was heated to 100 °C for 1 h. An I_2 solution (5 mg in 1 mL of acetic anhydride) was injected to the mixture and stirred for 25 min.

The product was purified *via* centrifugation with ethanol and freeze-dried from 1,4-dioxane. To measure the amount of the substituted acetyl groups, acetylated CNC (0.1 g) and an NaOH (0.5 N) solution (40 mL) were placed in a round flask, and the mixture was heated to 60 °C for 15 min. The mixture was then stirred at room temperature for 48 h. The amount of excess NaOH was back-titrated with 0.2 N HCl using phenolphthalein as an indicator. Using Equation S1, the amount of the substituted acetyl groups was calculated to be 5.03 mmol/g. Given the data, the conversion rate of the hydroxyl groups on the CNC surface into the initiators was estimated to be ~35 %.

S4. The surface and cross-sectional morphologies of the CNC-TFC-IP membrane

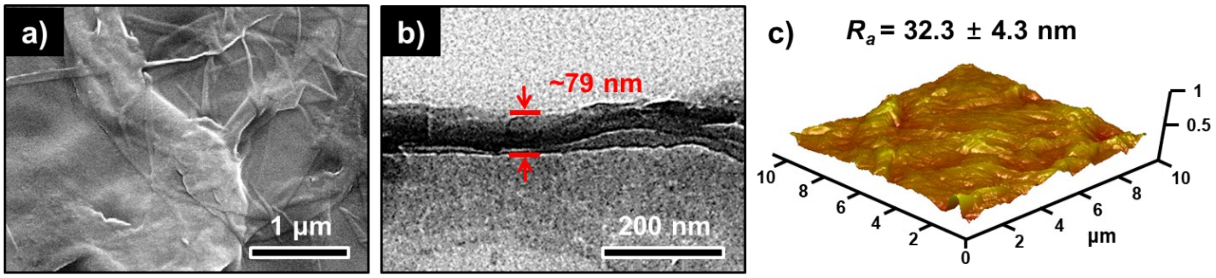

Fig. S2. (a) SEM surface, (b) TEM cross-section and (c) AFM surface images of the TFC membrane (CNC-TFC-IP) prepared using the CNC-PAH particles *via* the conventional IP method.

S5. Performance comparison

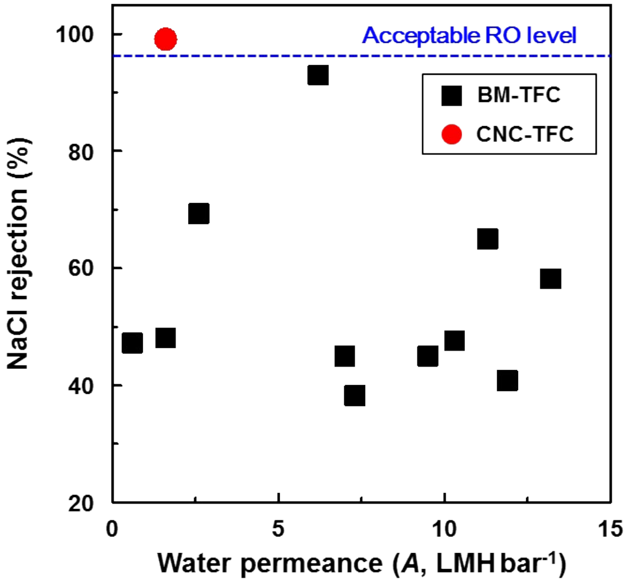

Fig. S3. Separation performance of the CNC-TFC membrane and other lab-made membranes (BM-TFC) prepared using various branched macromolecules (BMs) reported in the literature. NaCl rejection of the BM-TFC membranes is far below the acceptable RO level of NaCl rejection (~97%).

S6. XPS analysis of the membranes before and after the boric acid filtration test

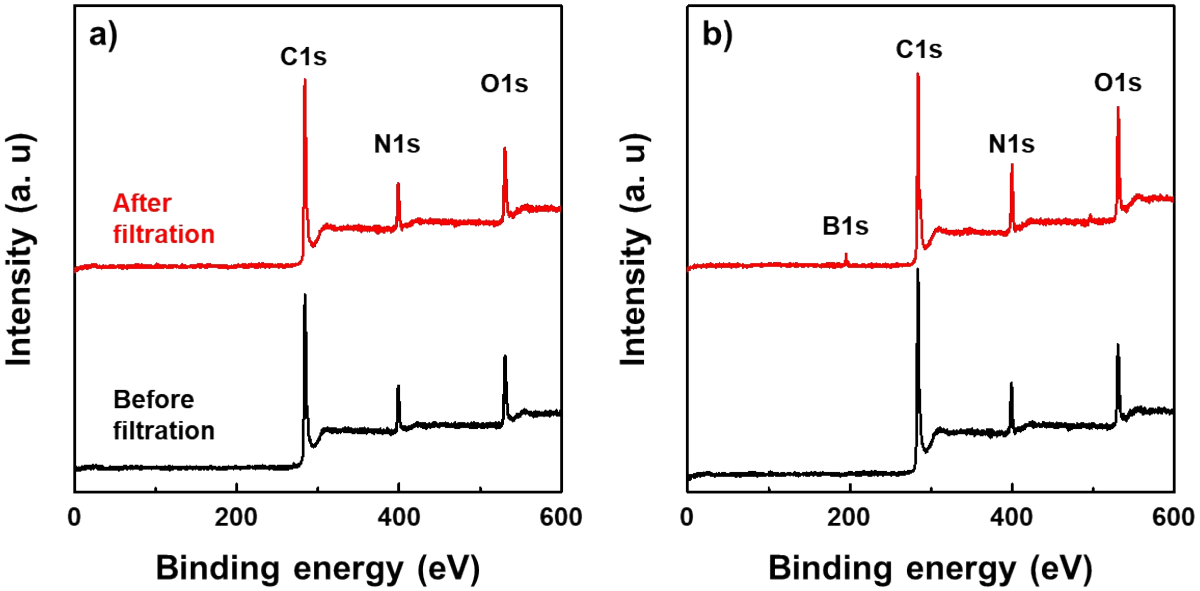

Fig. S4. XPS spectra of the (a) SWC4+ and (b) CNC-TFC membranes before and after filtration of the boric acid solution. After filtration, the B1s peak was observed only for CNC-TFC (not for SWC4+), indicating that some amount of boron (~0.5%) was captured in the CNC-TFC membrane.

S7. Long-term performance of the CNC-TFC membrane

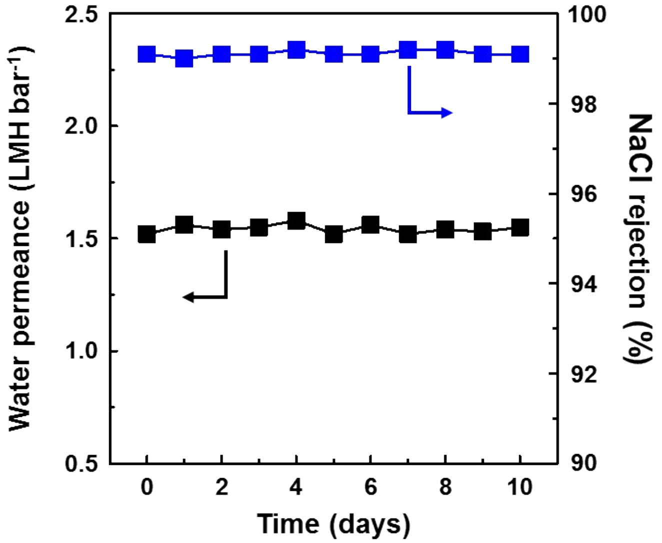

Fig. S5. Water permeance and NaCl rejection of the CNC-TFC membranes monitored for 10 days. Performance data were collected in a cross-flow filtration system with a NaCl (2000 ppm) aqueous solution at an operating pressure of 15.5 bar.

S8. Acid and base resistance of the CNC-TFC membrane

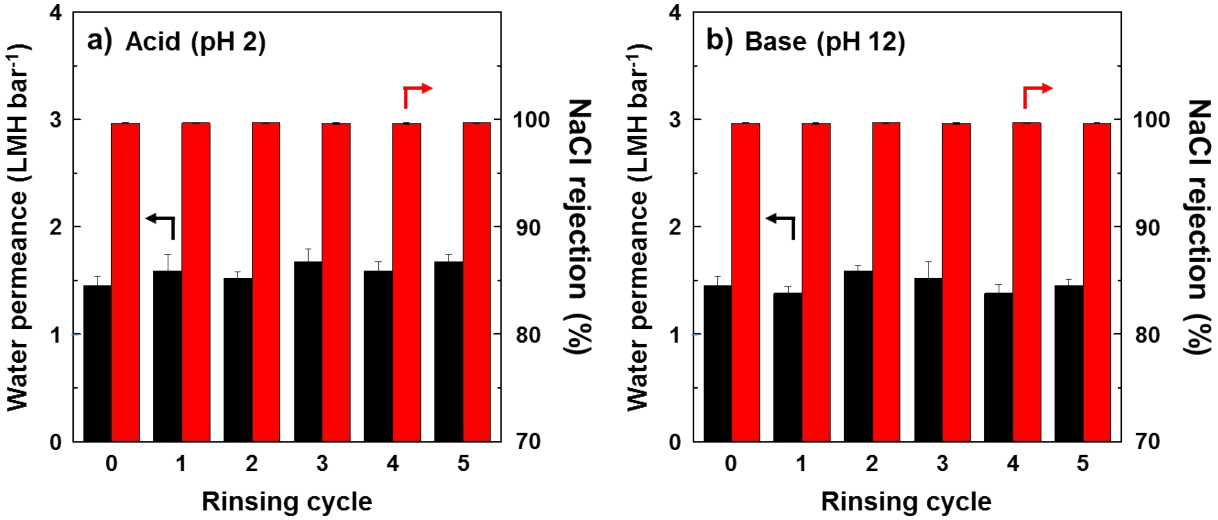

Fig. S6. Water permeance and NaCl rejection of the CNC-TFC membrane after (a) acid (pH 2) and (b) base (pH 12) treatments. Acid and base cleaning treatments were conducted in a cross-flow filtration apparatus by flushing the acid and alkali aqueous solutions, respectively, on the membrane surface at a pressure of 2 bar with a flow rate of 2 L min^{-1} for 15 min, followed by thorough rinsing with DI water. Performance data were collected in a cross-flow filtration system with a NaCl (2000 ppm) aqueous solution at an operating pressure of 15.5 bar.

References

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1 D. Kim, Y. Nishiyama, S. Kuga, *Cellulose*, 2002, **9**, 361.
2 E. Abraham, D. Kam, Y. Nevo, R. Slattegard, *ACS Appl. Mater. Interfaces*, 2016, **8**, 28086.