Supplementary Information

Zwitterionic Carbon Nanotube Assisted Thin-film Nanocomposite Membrane with Excellent Efficiency for Separation of Mono/Divalent Ions from Brackish Water

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1. Characterizations

The chemical compositions of CNT were probed by an X-ray photoelectron spectroscopy analysis (XPS, PHI Quantera II, Japan). The thermostability of CNT was studied by the thermogravimetric analysis (TGA, DTA Q600) over a temperature range from 50 to 700 °C in N_2 atmosphere, and the heating rate is 10 °C min^{-1}. The Zeta potential of nanoparticles were characterized by Zetasizer Nano ZS90 (British). Morphologies of CNT were investigated by transmission electron microscope (TEM, FEI Tecnai 20, America). The N_2 adsorption-desorption, BET surface areas and pore volumes of CNT were obtained by Micromeritics ASAP-2020 analyzer with high-purity nitrogen gas at -196 °C.

Field emission scanning electron microscopy (FE-SEM, FEI Quanta 250F, America) was used to observed the surface and cross-sections morphologies of membranes, and also the TEM (Hitachi H-7650, Japan) was used to study the cross-sections of the membrane which was sectioned to 70 nm thickness by Power-Tome-XL (America). The surface roughness analysis was conducted by atomic force microscope (AFM, broker Diension Icon, German) with 5 μm × 5 μm scanning range using intelligence mode.

Zeta potential of membranes surface was measured by an electrokinetic analyzer (SurPASS^{TM} 3 Anton Paar, Austria) at the pH scan from 3 to 10 adjusted by NaOH and HCl solution. Contact angle measurement device (*KRÜSS* DSA30, German) was used to measure contact angle of membrane. At least five measurements at different locations of each sample were conducted and averaged to get the WCA value.

2. Membrane Separation Performance Tests

Water flux and salt rejection of membrane were conducted in laboratory scale self-made cross-flow flat apparatus with an effective membrane area of 12.56 cm^2 [1]. The membranes were pre-pressurized at 1.0 MPa for 1 h to reach steady state before test. Afterwards, the pressure was maintained at 0.6 MPa with pure water or 1.0 g L^{-1} salt solution at room temperature.

The flux (J, L m^{-2} h^{-1}) of pure water or salt solution and the membrane rejection (R, %) were calculated on the basic of following equation:

$$J = \frac{V}{A\Delta t} \tag{1}$$

$$R = (1 - \frac{C_p}{C_f}) \times 100\% \tag{2}$$

where V is the volume of penetrate flow, A is the effective membrane area, Δt is the filtration time, C_p (mg L^{-1}) and C_f (mg L^{-1}) is the concentration of permeate and feed solutions, respectively. The concentration of salt solutions was determined by the electrical conductivity (UT30B, Shenzhen Uni-trend Electronics Company). All the membrane samples were repeated at least three times, and the results have been averaged.

The salt selectivity was calculated on the basic of following equation:

$$Selectivity(MgSO_4 / NaCl) = \frac{R_{MgSO_4}}{R_{NaCl}} \times 100\% \tag{3}$$

where R is the membrane rejection to MgSO$_4$ or NaCl.

Separation Performance of membranes in a series of salts concentration was conducted. 1 – 20 g L^{-1} of MgSO$_4$ and NaCl used as the typical feed solution, and the

flux and rejection is calculated on the basic of equation (1) and (2).

A simulated brackish water (as shown in Table S1)[2] was used to value the membrane separation performance. In order to achieve better separation of monovalent and divalent ion, two-stage NF membrane process was used in brackish water. The Na^+, Mg^{2+} and Ca^{2+} concentrations were obtained using the flame atomic absorption method (TAS-996, Beijing Purkinje General Instrument Co. Ltd., China), and an ion chromatography (DX-120, Dionex, USA) was used to measure Cl^- and SO_4^{2-} concentrations.

3. Anti-microbial property evaluation

The anti-microbial property of the membrane was investigated by measuring the growth status of *Escherichia coli* (*E. coli*) on the membrane as reported by Wang et. al [3]. At first, the membrane (12.56 cm^2) samples were placed in a petri dish and sterilized by UV irradiation for 1 h. Afterwards, 50 μL of diluted *E. coli* suspension (cell concentration is about 1×10^6 cfu/m^2) was loaded onto the surface of membrane sample, while ensuring the bacteria liquid was congruously contacted with membrane surface. The inoculated membrane placed in a 37 ^{o}C constant temperature incubator. After contacting for 2.5 h, the whole *E. coli* suspension was carefully collected by 5 mL normal saline and diluted 2-10 fold with normal saline. After that, 100 μL of diluent suspension were inoculated in LB agar medium and cultured in 37 ^{o}C constant temperature incubator. After culturing for 24 h, the viable bacteria colonies were counted.

The same procedure was also applied to the blank control group. *E. coli* suspension (cell concentration is about 1×10^6 cfu/m^2) which without being contacted with the membrane and were cultured in same condition for same time. And then, all the step is same to mentioned above. The mortality rate at a contact time was calculated by the following equation.

$$R = \frac{(B-A) \times 100}{B} \%$$

(4)

where R is the mortality rate at a contact time. A is the counted number of viable bacteria colonies after contacting membrane. B is the counted number of viable bacteria colonies without contacting membrane (blank control).

4. Anti-fouling performance evaluation

Anti-fouling performance were investigated by using bovine serum albumin (BSA) as the pollutant with a fixed concentration of 0.1 g L^{-1} at pH 7. The membranes were pre-pressurized under 1.0 MPa for 30 min, and then all of the permeation tests were carried out at 25 °C under 0.6 MPa. At first, 1 g L^{-1} mixed salts solution (0.5 g L^{-1} NaCl and 0.5 g L^{-1} MgSO$_4$) was filtered through the membrane for 30 min to obtain the initial water flux (J_0). And then, 0.1 g L^{-1} BSA and mixed salts solution were filtrated for 1 h to measure the flux under fouling. After that, the membranes were washed thoroughly with DI water for 1 h. The washing time was not counted in the filtration plots. Finally, 1 g L^{-1} mixed salts solution were filtered through the membrane again for 1 h. The 2 h filtration was defined as a filtration cycle. The anti-fouling performance assessment for each membrane was operated with 2 cycles. The flux recovery ratio

(*FRR*) was obtained from the equation:

$$FRR = \frac{J_t}{J_0} \times 100\%$$

(5)

where J_0 and J_t are the flux determined at the beginning and every 10 min in the

filtration process, respectively.

Table S1. Composition of the simulated brackish water samples.

Item	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
Concentration (mg L^{-1})	1102	200	100	1865	667
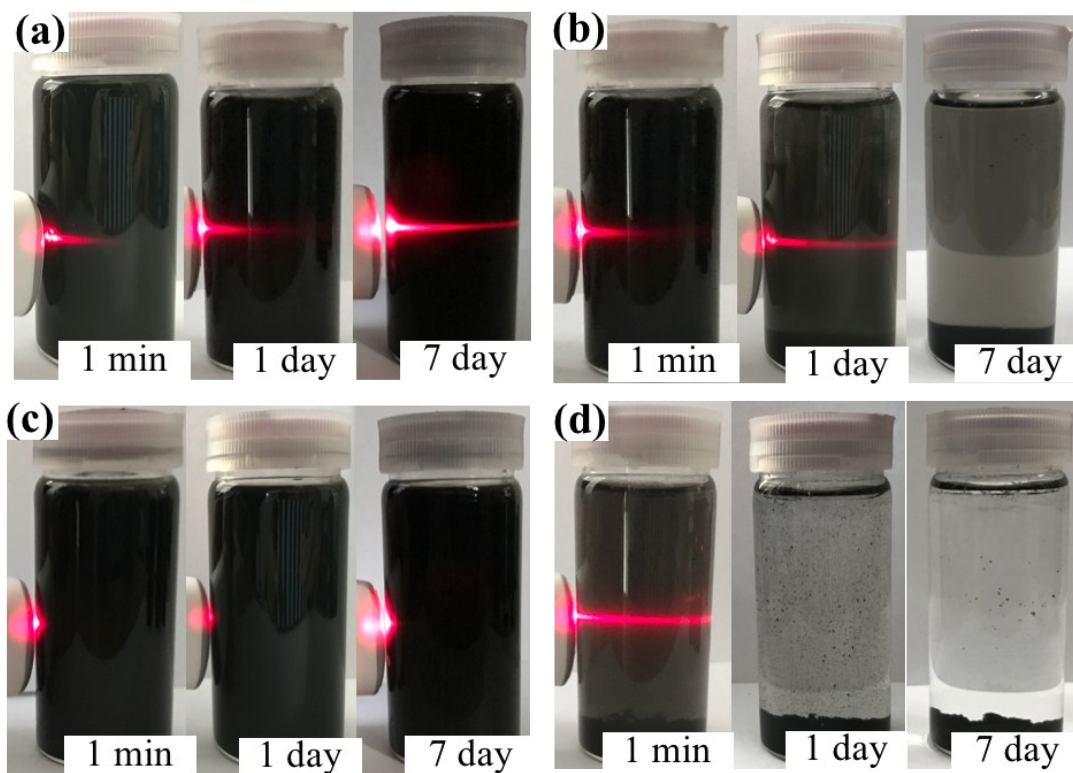
Figure S1. Photographs of 0.01 wt% fillers dispersed in water, after ultrasonication for 30 min under different pH conditions, (a) CNT-OH, pH = 11; (b) CNT-OH, pH = 3; (c) I-CNT, pH = 11; (d) I-CNT, pH = 3.
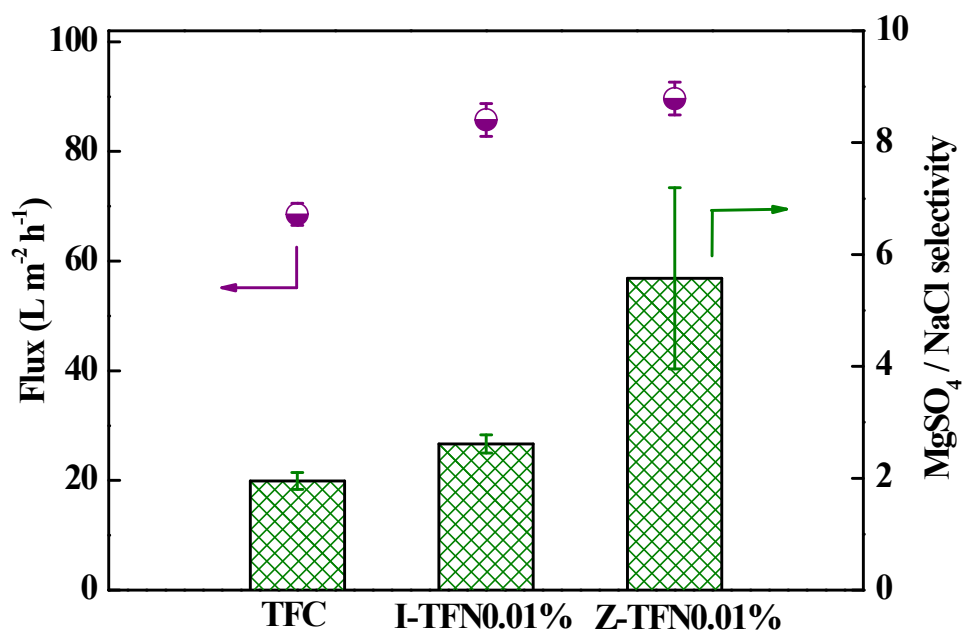
Figure S2. Separation performance of TFC, I-TFN0.01% and Z-TFN0.01% membranes (1 g L^{-1} NaCl and MgSO$_4$ aqueous solution) at 25 °C and 0.6 MPa

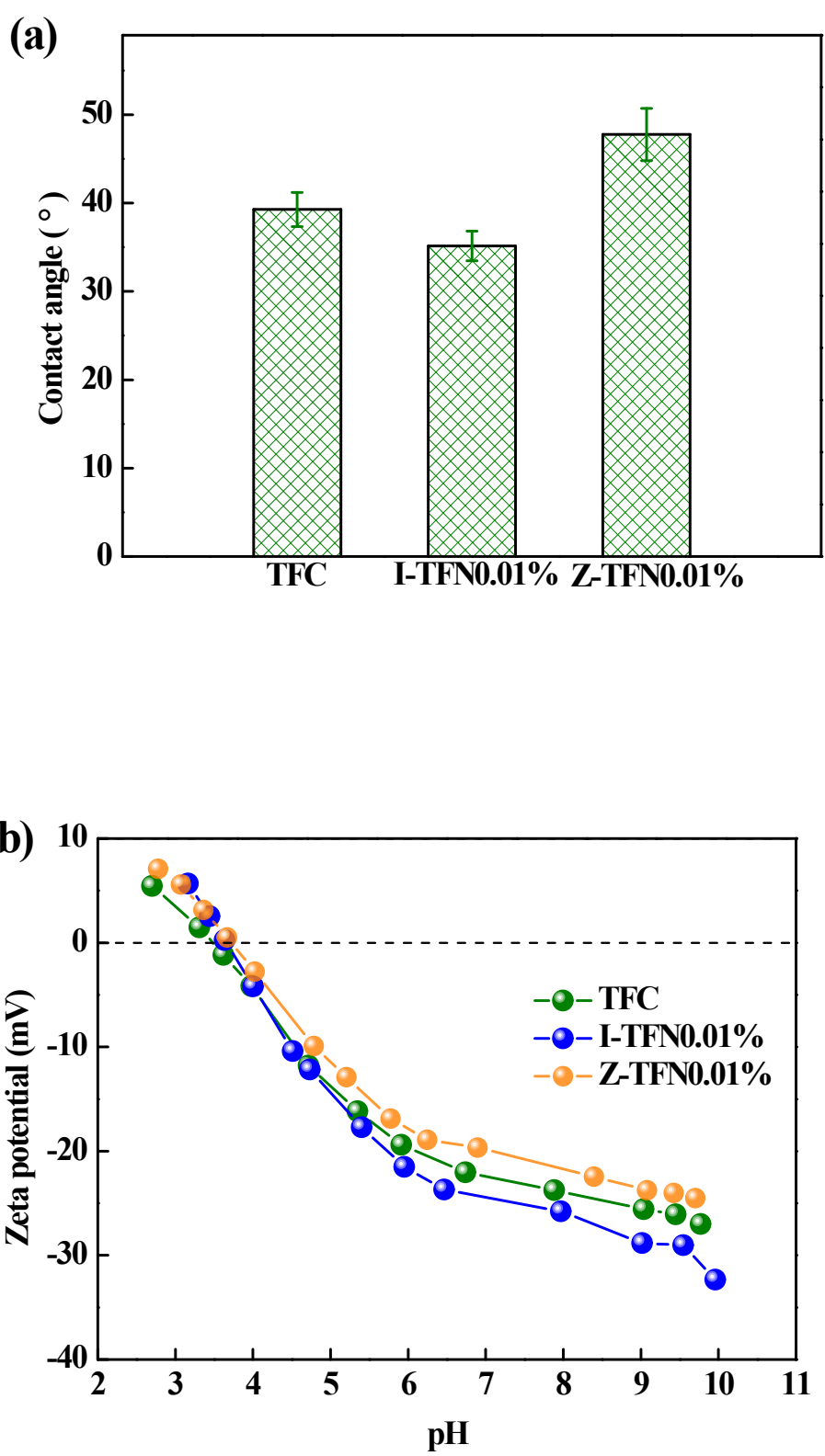**Figure S3.** (a) Water contact angles (contact time: 3 s) and (b) Zeta potentials at various pH values of TFC, I-TFN0.01%, and Z-TFN0.01% membranes.
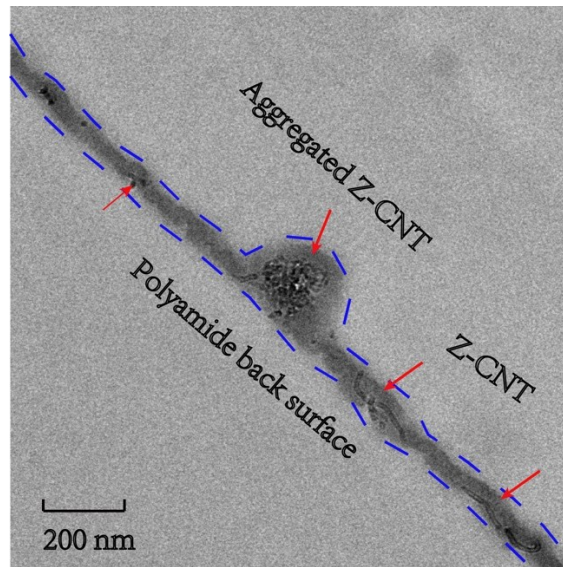
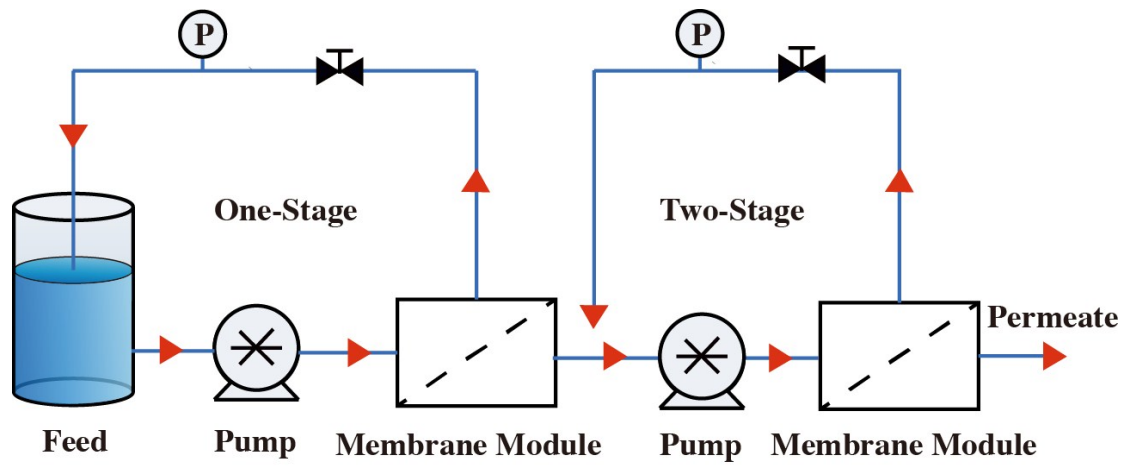**Figure S4**. Cross-section TEM images of Z-TFN0.05% membrane.

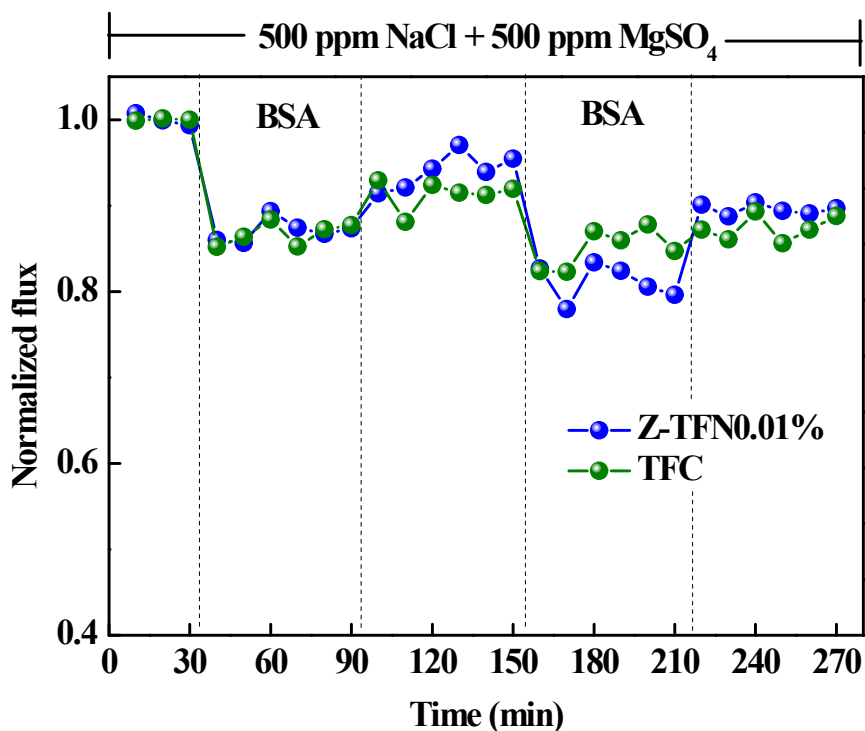**Figure S5.** Schematic picture of two-stage NF process for brackish water.

Figure S6. Short-term anti-fouling tests for TFC and Z-TFN0.01% membranes at 25 °C and 0.6 MPa. The feed solution contains 0.5 g L^{-1} NaCl, 0.5 g L^{-1} MgSO$_4$ and 0.1 g L^{-1} BSA.

As shown in Figure S6, both of the Z-TFN0.01% and TFC membrane possess excellent anti-fouling performance. More specifically, the FRRs for Z-TFN0.01% and TFC membrane reach to 89.6% and 87.4%, respectively, after the two-cycle test. It is generally believed that the resistance to the adhesion of pollutants could be enhanced by the enlargement of hydraulic layer[4-5]. In other words, the surface hydrophilicity exerts great influence on the anti-fouling property. As indicated from Figure S3 (a) and (b), both Z-TFN0.01% and TFC membrane show quite similar water contact angles and Zeta potential curves, which in turn results in the similar level of the anti-fouling properties of the two membranes. The reason is probably due to the low dosage of fillers (0.01% in the aqueous solution), which may not quite affect the surface wettability.

References

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