Effective Antiscalning Performance of Reverse-Osmosis Membranes
Made of Carbon Nanotubes and Polyamide Nanocomposites

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ABSTRACT: The antiscalning properties of multiwalled carbon nanotube (MWCNT)–polyamide (PA) nanocomposite reverse-osmosis (RO) desalination membranes (MWCNT–PA membranes) were studied. An aqueous solution of calcium chloride (CaCl₂) and sodium bicarbonate (NaHCO₃) was used to precipitate in situ calcium carbonate (CaCO₃) to emulate scaling. The MWCNT contents of the studied nanocomposite membranes prepared by interfacial polymerization ranged from 0 wt % (plain PA) to 25 wt %. The inorganic antiscalning performances were compared for the MWCNT–PA membranes to laboratory-made plain and commercial PA-based RO membranes. The scaling process on the membrane surface was monitored by fluorescence microscopy after labeling the scale with a fluorescent dye. The deposited scale on the MWCNT–PA membrane was less abundant and more easily detached by the shear stress under cross-flow compared to other membranes. Molecular dynamics simulations revealed that the attraction of Ca²⁺ ions was hindered by the interfacial water layer formed on the surface of the MWCNT. Together, our findings revealed that the observed outstanding antiscalning performance of MWCNT–PA membranes results from (i) a smooth surface morphology, (ii) a low surface charge, and (iii) the formation of an interfacial water layer. The MWCNT–PA membranes described herein are advantageous for water treatment.

INTRODUCTION

Reverse-osmosis (RO) membranes based on aromatic polyamide (PA) have been extensively used to provide clean water by purification and desalination because of their high-cost efficiency, high-volume water production, and reasonably simple operation. However, fouling is still the main cause of the undesirable decrease in permeate flux, which results in an increased energy consumption during RO membrane’s operation. In addition, the necessary periodic membrane cleaning process interrupts the continuous operation of the purification or desalination. Although organic fouling can be largely reduced by using a nanofiltration pretreatment process, it is difficult to prevent the deposition of inorganic foulant, also known as “scale”. Scale is precipitated from the ions such as Ca²⁺ and CO₃²⁻ in the feed water that, unlike organic foulants such as carbohydrate polymers or proteins, are not completely removed by nanofiltration because of their small size (Figure S1). To maintain the membrane performance against inorganic scaling, membrane cleaning and pretreatments involving the use of antiscalants are periodically carried out to prolong the membrane lifetime. Therefore, water treatment technology requires robust RO membranes with improved antifouling/antiscalning properties to lower the maintenance costs and save energy in large-scale water desalination processes. In addition, reducing the use of antiscalning additives during membrane pretreatments has been encouraged recently to decrease the impact of desalination plants on the environment. For these reasons, RO membranes with antiscalning properties are becoming more and more important in efforts to prevent serious fouling and to improve environmentally friendly water desalination processes.

In general, organic foulants can cause serious problems because of their strong adhesion. On the contrary, inorganic scaling by itself is not considered as a serious issue because it is washable by using dilute acid solutions. Although scaling generally does not damage the membrane, the scale accumulation decreases the membrane performance and promotes organic fouling. Indeed, in the presence of calcium the hydrophobicity of the membranes increases and results in the formation of denser and thicker complex fouling layers in combination with organic foulants, which are difficult to remove even with acidic solutions. A promising...
approach to improve the antifouling properties of PA is to incorporate multiwalled carbon nanotube (MWCNT) to the membranes. It has been found that additions as low as 0.001% and as high as 15.5 wt % of MWCNT to PA membrane improved not only the permeate flux but also the antifouling properties against BSA, reduced the scaling by sea salt, mainly by reducing the surface roughness and increasing the membrane hydrophilicity.1,20,21

In recent years, computational studies of membranes have improved considerably in part because of the increased availability of computer resources. Molecular dynamics (MD) simulations have been mainly used to calculate water diffusion and salt rejection22 and lately to study protein fouling.20 Organic fouling is a polymer–polymer simulation and thus is relatively easy to simulate. However, inorganic scaling is a complex problem because it involves the simulation between solvated ions, a phase change, the PA structure, and water. The homogeneous nucleation of CaCO3 in solution by itself is already a complex problem that has been approached using both ab initio23,24 and classical MD methods.25,26 Although ab initio techniques can be more accurate to compute the energy and stability of the prenucleation CaCO3 clusters, it is limited to a few tens of atoms and thus cannot be used to simulate the interaction with the membrane structure. In the last years, new force fields with increased precision have allowed to simulate the homogeneous nucleation of CaCO3 by using MD with very good results. In the present work, we have used the theoretic framework developed by Raiteri and Gale25,26 to simulate the homogeneous nucleation of CaCO3 and applied it to simulate the effect of the PA structure on the stability of amorphous CaCO3 (ACC) clusters. In this work, we used the theoretic framework developed by Raiteri and Gale to develop a novel approach to simulate the scaling on PA and MWCNT–PA membranes. We also evaluated the antiscalant performance of MWCNT–PA membranes against CaCO3 by in situ fluorescence microscopy (FM), scanning electron microscopy (SEM), and permeation measurements. In addition, we performed MD simulations to gain insights into the mechanism of scale nucleation. Finally, we propose a possible mechanism for antiscaling nanocomposite membranes. The combined experiment and simulation results enabled a better understanding of the antiscalant mechanism in MWCNT–PA membrane.

## RESULTS AND DISCUSSION

### Antiscalant Performance of the MWCNT–PA Nanocomposite Membrane Studied by Water Permeation

The permeate flux J and salt rejection values R of each membrane including the MWCNT–PA membrane with 15.5 wt % MWCNT under typical desalination conditions are summarized in Table 1. On the basis of those performances, we chose three types of membranes having comparable properties for the present antiscalant study. The trade-off between salt rejection and permeation in desalination membranes is well-known, and there are reports27 of MWCNT–PA membranes with higher permeate flux but lower salt rejection, that is, 19.2 L m⁻² h⁻¹ and 98.2% salt rejection compared to the 8.7 L m⁻² h⁻¹ and 99.8% salt rejection by our MWCNT–PA. In this study, the MWCNT–PA membrane with 15.5 wt % MWCNT was studied because of the rejection and permeation similar to that of the CM-PA membranes.

Figure 1 shows the changes in the value of $J(t)$ of each membrane during cross-flow filtration, evaluated as a function of time after the addition of the scaling precursors. The periodical fluctuations seen every 24 h are caused by the adjustment of salinity, but these perturbations are small compared with the long-term trends. All of the membranes studied showed a drastic decrease to approx. 60–75% of the starting permeation quickly after the scaling process started. Subsequently, the flux remained at the same level in cases of the lab-PA membrane (0 wt % MWCNT), CM-PA, and MWCNT–PA membranes with a MWCNT content of 13 wt % or lower.

Permeate fluxes gradually recover up to 95 ± 2% of the starting values on the nanocomposite membranes containing more than 15.5 wt % of MWCNTs. The recovered fluxes $J(t)$ were 97% for 15.5 and 20 wt % MWCNTs and 94% for 25 wt % MWCNTs. The reason of the different scaling properties of the membranes containing above 13 wt % might be in part because of a volumetric percolation effect of the MWCNTs. The addition of MWCNT slightly decreased the salt rejection, whereas the permeate flux increased. We therefore selected the membranes containing 15.5 wt % of MWCNTs as the representative with the highest salt rejection among the studied MWCNT–PA membranes.

### In Situ Scale Formation Monitored by FM

Figure 2a–c is a series of FM images of each membrane every 12 h during a

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**Table 1. Permeate Flux and Salt Rejection of Each RO Membrane Used for the Scaling Study at 0.7 MPa and 500 mL/min Cross-flow Experiments Using 0.06 wt % NaCl Aqueous Solution**

| RO membrane         | permeate flux, J/L m⁻² h⁻¹ | salt rejection, R/\% |
|---------------------|---------------------------|----------------------|
| MWCNT–PA membrane  | 8.7                       | 99.8                 |
| (15.5 wt % MWCNT)   |                           |                      |
| Lab-PA membrane     | 7.9                       | 99.7                 |
| commercial membrane (CM-PA) | 9.2                  | 99.8                 |

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48 h period during the scaling study. Fluorescence quenching caused by the MWCNT embedded in the membranes was negligible (Figure S2). The initial control image shows that the fluorescence from the membrane itself, the additives, the acrylic cell, and the spacer is low enough to avoid interference with the fluorescence of the dyed scale. Thus, the green fluorescence in the following frames is originated from the CaCO₃ scale deposited on the membrane surfaces.

After 12 h of scaling, the CaCO₃ deposited preferentially at the gap between the membrane and the spacer, where the water flow stagnated. The scale was visible through the transparent polypropylene spacer (Figure S3). The onset of the fluorescence signal from the CaCO₃ was as short as 12 h on the lab-PA and CM-PA. Particularly, fluorescence from the CM-PA was intense, and a deposition pattern that was identified (see arrows at the upper and lower part in the area enclosed by the spacer in Figure 2c) remained after 48 h, and the fluorescence signal intensity increased with time because of the gradual growth of scale deposition. The lab-PA and CM-PA exhibited homogeneous scaling, as indicated by the overall fluorescent green signal from the entire membrane, even though the scaling patterns of the lab-PA (Figure 2a) were not so clear as that of CM-PA (Figure 2b) at 48 h. These scaling patterns were probably originated from the turbulent flow pattern caused by the spacer.⁴⁸

On the other hand, the amount of scale deposited on the MWCNT–PA membranes was much lower than that on CM-PA, revealing an intrinsic antiscaling property. Figure 2d shows the quantified fluorescence signal from the membrane surfaces by scale deposition. There were slight differences on fluorescence of each samples which were not yet exposed to scale-forming solution (t = 0 h). Therefore, the fluorescence intensity was normalized relative to that of the pristine membrane (t = 0 h) to eliminate the influence of the background. No increase in the fluorescence intensity was observed on the MWCNT–PA membranes. The microscopic examination of the membrane surfaces shows the absence of large-scale particles after 12 h; thus, the drastic Jᵣ(t) decrease, as shown in Figure 1, suggests the clogging of the water channel on the membrane with small particles (a few nanometers in diameter, that is, too small for the optical microscope resolution) by instantaneous scale formation.

Figure 3a,e is the FM snapshots of the membranes after 48 h of scaling. The CaCO₃ deposited on the membrane surface was confirmed on all membranes. The fluorescence signal from the MWCNT–PA membranes was considerably lower compared to the signal from the other membranes. The sudden disappearance of the green spots of fluorescence (circles in Figure 3a,b) after exposure to a water flow of 500 mL/min during additional 4 h indicates scale detachment in the MWCNT–PA membrane. This is an important and advantageous characteristic of the MWCNT–PA membranes.

![Figure 2. FM images of the membrane surface with the spacer as a function of scale-deposition time t in the cross-flow experiment at 0–48 h. (a) MWCNT–PA, (b) lab-PA, and (c) CM-PA membrane. The arrows indicate representative figures of scale deposition. (d) Averaged normalized fluorescence intensity from the RO membrane images shown in (a–d) (the spacer was not included for the intensity counting) as a function of scaling time.](image-url)

![Figure 3. FM snapshots of the MWCNT–PA (a,b), lab-PA (c,d), and CM-PA (e,f) after additional 4 h of cross-flow operation under scaling conditions. Scale formation (a) and spontaneous detachment (b) were observed at the marked regions by circles with numbers on the MWCNT–PA membrane.](image-url)
Interestingly, no scale detachment was observed on the lab-PA and CM-PA (Figure 3d,f).

Our FM observations revealed that the scale deposited on the membranes and around the spacer could be removed by acid washing using a 5.0 vol % of acetic acid (Figure S4). The acid washing did not modify the scaling behavior of each membrane, and the second and third scaling cycles resulted in patterns and fluorescence intensity similar to those in the first cycle.

**Relationship between Membrane Surface Morphology and Scaling.** Figure 4a–c includes SEM images of the surface of each pristine membrane. MWCNT–PA membrane shows a relatively smooth surface, whereas the lab-PA and CM-PA membranes have a typical ridge-and-valley morphology. Atomic force microscopy (AFM) observations confirmed that the roughness of the MWCNT–PA membrane was smaller. The membrane with higher surface area provided by such ridge-and-valley structures has a higher permeate flux and salt rejection, although it is likely that surface roughness could trigger scale deposition. By increasing the MWCNT content up to 15.5 wt % (Figure 4a), the surface became much smoother than that of the plain PA membranes.

SEM images of the membrane surface at low (Figure 4d–f) and high (Figure 4g–i) magnifications are shown for the samples after 52 h of scaling deposition. As shown in the figures, the surface of the MWCNT–PA is cleaner than the surfaces of the lab-PA and CM-PA with a scale, as indicated by arrows in the figures. All samples show a small quantity of well-defined cubic crystals of CaCO₃, as confirmed by energy-dispersive X-ray (EDX) analysis (Figure S5).

Our SEM observations revealed agglomerates consisting of minute spherical particles (10–50 nm; Figure S6), which appear as typical ACC. Those ACC particles tended to grow by clinging within the ridge-and-valley structures in the lab-PA and CM-PA (Figure 4h,i). This is consistent with the observation that ACC tends to be more stable in confined niches. On the contrary, ACC was less abundant on the MWCNT–PA membrane (Figure 4g) most likely because of its smooth surface. ACC scaling also grew around the crystalline CaCO₃ on CM-PA. Strong fluorescence intensity from the CM-PA, as shown above (Figure 2), is presumably because of the formation of both crystalline CaCO₃ and ACC. Indeed, the formation of both phases is common as ACC spontaneously transforms to a stable crystalline form at ambient temperatures.

The smoother surface of the MWCNT–PA membranes promoted the growth of crystalline CaCO₃ rather than ACC; when compared with the fluorescence observations, a preferential dying of ACC was found. The deposited crystalline CaCO₃ was easily detached by the water flow when the size of the crystals became large, as shown in Figure 3. Our observations correlating roughness and scale deposition confirm the previous report that the membranes with higher roughness are prone to scale formation.

Static heterogeneous nucleation study (Supporting Information section S1.1) showed that the amount of formed CaCO₃ was greater, and particle sizes are larger on the lab-PA membrane (Figure S7a) compared to the MWCNT–PA membranes (Figure S7b). These results confirm an intrinsic antiscaling behavior of the MWCNT–PA membranes, in agreement with the cross-flow experiments.

**Effect of Membrane Surface Charge on Scaling.** Anionic membranes with a negatively charged surface promote more inorganic scaling by the ionic attraction than cationic membranes. Surface charge analysis by zeta potential measurements can thus provide a more precise understanding of the scaling mechanism. Figure 5 shows the zeta potential of the membranes plotted as a function of pH. The MWCNT–PA was approx. 20–30 mV less negatively charged compared to the lab-PA and CM-PA in the pH range from 4.5 to 9.0. The negative surface charge in PA membranes is originated from the hydrolysis of unreacted acyl chloride that convert to carboxyl groups. The effect of MWCNT to the formation of carboxyl groups is unclear; however, we propose that it might be related to the stiffening of the PA structure that might avoid the migration of these hydrophilic and negatively charged groups to the membrane surface. This might be an advantageous feature of the MWCNT–PA membranes because less negatively charged surfaces have weaker electrostatic attraction toward Ca²⁺ ions near the membrane surface, thereby reducing nucleation rate of CaCO₃.

**MD Simulation.** The MWCNTs used here (with approx. 10 nm diam) in PA are much larger compared to CaCO₃ clusters (approx. 0.4–1.0 nm in size). Therefore, a flat graphitic sheet, or single-layer graphene, can be used to simulate the MWCNT surface, as reported in the literature. After running a charge-transfer calculation in the graphene-PA (G-PA), the total charge of the PA became positive +4.65e, and the
graphene total charge is negative, $-4.65e$. These results are shown in Figure S8, in which (a) an MD snapshot and (b) a charge-density map of the G-PA model with graphene (positioned at $Z = 0.0$ nm) are shown. The magnitude of the charge transfer from PA to graphene is particularly strong above the surface of graphene (approx. $Z = 0.5 - 1.0$ nm), and it gradually decreases at distances $>1.0$ nm from the graphene.

The main contribution of charge transfer is because of the electron transfer from the PA-aromatic rings to the graphene sheet. Similar charge transfer behavior was observed for the MWCNT–PA model as well (Figure S8c,d). The electron transfer from PA to the MWCNT results in a total negative charge of $−3.21e$, and the total PA charge increases to a positive charge of $+3.21e$. Therefore, the use of the G-PA model is adequate when simulating the antiscaling behavior of MWCNT–PA.

The water molecules are bound to the G-PA and PA surface by hydrogen bonds. Figure 6 shows water molecules on (a) G-PA and (b) plain PA surface. White: hydrogen atoms of water. Red: oxygen atoms of water. Purple: PA molecules. MD snapshots of CaCO$_3$ clusters above the surface of G-PA after (c) 3 and (d) 20 ns, plain PA after (e) 3 and (f) 20 ns. Water molecules were considered for the simulations but not present in the figure. (g) CaCO$_3$ potential energy above G-PA or plain PA with simulation time. PA and (b) PA. The average number of water molecules per unit area was 19.2 nm$^{-2}$ for G-PA and 11.7 nm$^{-2}$ for PA. This well-packed and homogeneous water layer on G-PA is known as the interfacial water layer. As supported by the zeta potential measurement, G-PA surface has a weaker negative charge that tends to interfere with oxygen lone pairs of water molecules, resulting in the attraction of more water molecules and the shielding of amide bonds within the membrane surface (blue spheres). Therefore, facing-up hydrogen atoms of the interfacial water layer are abundant on the G-PA, where the white areas correspond to hydrogen atoms, as shown in Figure 6a,b. The higher affinity of the membrane surface for water molecules can be partially responsible for the higher wettability shown by contact angle measurements of the MWCNT–PA membrane ($40.1 \pm 3.8^{\circ}$) compared to the lab-PA membrane ($47.7 \pm 3.6^{\circ}$).

During the scale formation, the nucleation of CaCO$_3$ is driven by strong Coulomb interactions between Ca$^{2+}$ and CO$_3^{2-}$ in aqueous solutions on the membranes. At an initial state, CaCO$_3$ is nucleated as an amorphous solid, followed by the adsorption of CaCO$_3$ molecules on the membranes. We performed the MD calculations with the NPT ensemble by applying 1 atm. Figure 6c–f includes MD snapshots after 3 and 20 ns for CaCO$_3$ formation above G-PA or plain PA. The nuclei of ACC (yellow dashed circles in Figure 6c) were approached and drifted near the G-PA surface after 3 ns. After 20 ns, CaCO$_3$ crystals were located away from the G-PA surface (Figure 6d). This result indicates weak interaction between the CaCO$_3$ and the G-PA surface. On the other hand, in terms of CaCO$_3$ above plain PA, CaCO$_3$ approached (i) and then combined with a second CaCO$_3$ molecule (ii) after 3 ns (Figure 6e). A protonucleus of CaCO$_3$ was still stable on the surface of PA after 20 ns (Figure 6f). These MD simulations showed that CaCO$_3$ interacts stronger with the plain PA surface compared to G-PA.

Strong Coulomb interactions occurring between the CaCO$_3$ nucleus and water molecules result in rigid water shells. Figure 6g shows the CaCO$_3$ potential energy involving Coulomb and van der Waals energies with simulation time. For the initial simulation time, less than 2 ns, the potential energy decreases quickly. This large potential decrease corresponds to the formation of CaCO$_3$ nuclei, and the energy gradually decreases after 2 ns. The average potential energy of CaCO$_3$ on plain PA at 20 ns was $-47.91$ (kcal/mol), whereas that of G-PA was $104.68$ (kcal/mol). These results suggest a highly stable adsorption of CaCO$_3$ on plain PA membranes, which would result in scale formation and accumulation. Furthermore, these results are also consistent with the fact that CaCO$_3$ structures are more stable in confinement. CaCO$_3$ clusters are stacked on the surface of plain PA and grow by aggregating with other CaCO$_3$ clusters (Figure 6e,f). From the multiscale viewpoint, our results are consistent with the observation that ACC preferentially forms in confined niches even at the microscopic level.

Radial distribution functions are shown in Figure 7. For the CaCO$_3$ formation, Ca$^{2+}$ interacts strongly with water than CO$_3^{2-}$ at the hydration state. Therefore, the simulation was focused on the interaction between Ca$^{2+}$ and water. Figure 7a illustrates the radial distribution function between Ca$^{2+}$ and the oxygen of water molecules. A sharp peak at 0.23 nm indicates the presence of a strong first hydration shell. The distribution peak of the first hydration shell is larger in the G-PA model compared to the plain PA. It is interesting to note that the Ca$^{2+}$ located adjacent to the membrane was influenced by the membrane, and the first hydration shell was formed around Ca$^{2+}$. For G-PA, Ca$^{2+}$ had a more rigid water shell according to MD simulations. The rigid hydration shell (interfacial water) is formed by a water-shielding effect from the PA amide bonds. Figure 7b shows the radial distribution function between oxygen of PA amide bonds and hydrogen of water molecules. The amide bonds of PA in G-PA were surrounded by several water molecules (interfacial water layer composed of first and second hydration layers), resulting in the shield of PA amide bonds from the interaction with Ca$^{2+}$. The first and second hydration layers formed were 0.35 nm thick (Figure 7b).
shielding effect of the interfacial water layer on G-PA was larger than that on the plain PA membrane. In fact, a radial distribution peak between Ca\(^{2+}\) and the oxygen of PA amide bond existed in the plain PA membranes but was absent in G-PA (Figure 7c). This means that Ca\(^{2+}\) is strongly attracted to a plain PA surface compared to the G-PA model. The water-shielding effect, which is associated with the formation of interfacial water on G-PA, effectively provides antiscaling behavior to the membrane surface by weakening the interaction between PA amide bonds and CaCO\(_3\) individual molecules and clusters.

The inorganic scale surrounded by the interfacial water layer, formed by the stronger hydration interaction, weakens the adsorption potential of CaCO\(_3\) to the membrane surface. We performed MD step trajectory mapping with one CaCO\(_3\) molecule and an ACC form constructed by 50 CaCO\(_3\) molecules for 5 ns.

Figure 8 shows the center of mass trajectory of CaCO\(_3\) and the atomic density of PA (in gray). Figure 8a,b shows one CaCO\(_3\) trajectory of the G-PA model and one of the plain PA, respectively. In both cases, CaCO\(_3\) drifts near the membrane surfaces. However, it is important to note that CaCO\(_3\) had a higher mobility above the surface of G-PA with time (Figure 8a) when compared to plain PA. The diffusion coefficient of one CaCO\(_3\) was 2.55 × 10\(^{-6}\) cm\(^2\) s\(^{-1}\) on G-PA and 0.42 × 10\(^{-6}\) cm\(^2\) s\(^{-1}\) on plain PA.\(^{46}\) The MD trajectory for ACC (n = 50) of G-PA and plain PA are shown in Figure 8c,d. The diffusion coefficient of ACC was 0.69 × 10\(^{-6}\) cm\(^2\) s\(^{-1}\) on G-PA and 0.11 × 10\(^{-6}\) cm\(^2\) s\(^{-1}\) on plain PA. ACC above the surface of G-PA model also widely drifts compared to plain PA and stays away from the G-PA surface after 4 ns because of the weak interactions occurring between ACC and PA.

### CONCLUSIONS

MWCNT–PA membranes synthesized with MWCNT content up to 25 wt % were studied for inorganic antiscaling performance, and the CaCO\(_3\) deposition was monitored in situ by FM. The MWCNT–PA membrane containing 15.5 wt % of MWCNT showed antiscaling properties in addition to a lower decrease in water permeability during the scale tests compared to other PA-based membranes and interestingly showed a gradual recovery of the water flow because of scale detachment. This outstanding antiscaling performance of the MWCNT–PA membrane was caused by smoother surface, less negatively charged surface than other PA-based membranes, and the induction of an interfacial water layer on the MWCNT–PA membrane surface. Small loadings of MWCNT did not affect the surface morphology of the membrane nor did they restrict the mobility of the PA network. Also, the results show that approximately 15 wt % of MWCNT is necessary to substantially modify the PA properties. Our MWCNT–PA membrane with superior antiscaling properties may be highly advantageous when operating in harsh conditions such as water containing large amounts of inorganic moieties. These membranes can be applicable not only for desalination but also for groundwater, industrial water, and sewage treatment.

### EXPERIMENTAL SECTION

**Materials.** m-Phenylenediamine (MPD, >98%) and trimethylsilyl chloride (TMC, >98%) were purchased from Tokyo Chemical Industry Co., Inc. (Tokyo). Hexane (>96%) and sodium bicarbonate (>99%) were acquired from Kanto Chemical Co., Inc. (Tokyo). MWCNTs (NC-7000 from Nanocyl) dispersion was purchased from KJ Specialty Paper Co., Ltd. (Shizuoka, Japan). Anhydrous CaCl\(_2\) (>95%) and NaCl (>99.5%) were purchased from Wako Co., Ltd. (Osaka, Japan). Calcein was purchased from Dojindo Molecular Technologies, Inc. (Kumamoto, Japan).

**Reverse Osmosis Membranes Preparation.** MWCNT–PA membranes containing variable amounts of MWCNT (ranging from 5 to 25 wt %), laboratory-made plain PA (lab-PA) membranes (0 wt % of MWCNT), and one of the typical commercial RO PA (CM-PA) membranes were studied. The lab-PA membranes and the MWCNT–PA membranes were prepared by interfacial polymerization processes as previously described.\(^{45}\) Typically, porous polysulfone substrates were soaked in a dispersion of MWCNT in an MPD aqueous solution, and the excess liquid was drained. The support membranes were then immersed in TMC solution in hexane, and the interfacial polymerization took place. The different MWCNT contents in the PA were controlled by changing the MWCNT concentration in the MPD aqueous solution. The
presence of MWCNT within the membrane was confirmed by SEM observation in peeled-off RO active layer (Figure S9a) and through an induced crack in the RO active layer (Figure S9b). Addition of nanotubes during the PA synthesis usually decreases the roughness of the resulting PA membranes, as it can be seen by comparing the AFM images provided in Figure S9c,d. The plain PA membrane shows a roughness ($R_g$) of 37.2 nm compared to the 28.2 nm of the MWCNT–PA membrane. We studied in detail the MWCNT content in the nano-composite membranes and its effect on the morphology and chlorine resistance in a recent publication.47

Cross-flow Filtration Experiments. The schematic illustration of the experimental system is shown in Figure S10a. A cross-flow filtration system (FTU-1, Membrane Solutions Technology, Tokyo) was operated at 0.7 MPa with a flow rate of 500 mL/min through the cross-flow cell. The membrane used for the study was diam 25.0 mm (MWCNT–PA and lab-PA membranes were shown as examples in Figure S10b,c). A custom-made transparent acrylic crossflow cell (diam 25.0 mm, height 0.356 mm in the cell chamber; Figure S10d) with an effective membrane surface area of 3.46 cm² was used to monitor the membrane surface by FM. A spacer (1.2 mm thick, GE Water & Process Technologies, Trevose, PA, USA) was placed on the membrane surface (Figure S10e) to replicate the typical flow patterns in the large-scale RO modules, and the water source was kept at 21 ± 1 °C and pH8 during all experiments. Aqueous solutions of NaCl (0.06 wt %) were used for the initial compaction process. Salinity and pH were adjusted every 24 h to keep constant during the long-term test. Relatively low NaCl concentration and pressure were chosen for the scaling study because the acrylic cross-flow cell has an upper pressure operation limit of 1 MPa. Dark spots observed in Figure S10e are associated with high local concentration of MWCNT in the PA membrane. The NaCl rejection, $R$ (%), and permeate flux, $J$ (L m⁻² h⁻¹) were derived using an electrical conductivity meter and a balance, respectively. The normalized flux $J_r(t)$ was defined to evaluate the permeate flux change. Details are available in Supporting Information section S1.2. The SEM images (top and side views, Figure S10f,g) of the spacers showed that threads in one direction (labeled i) supported on the RO membrane surface, whereas the threads in the other direction (ii) lie on top of the other threads without contacting the membrane. The concentration of the aqueous mixture was determined as described in the literature.56 After compaction of the membrane in the cross-flow, CaCl₂ (1000 ppm) and NaHCO₃ (100 ppm) were dissolved in NaCl aqueous solution (0.06 wt %). The basic chemical reaction of CaCl₂ and NaHCO₃ can be written as follows:

$$\text{CaCl}_2 + 2\text{NaHCO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$$  (1)

CaCO₃ is insoluble in water, and it consequently precipitates both in solution and on the surface of the membrane, thus resulting in scale formation.

Membrane Characterization. Each pristine membrane and scale-deposited membrane were observed by SEM using an SU8000 (Hitachi, Tokyo) operated at 1.0 kV of the acceleration voltage. The samples were coated with platinum (approx. 1.0 nm thickness) to avoid surface charging during the observation. An EDX analysis using the same instrument was conducted. For FM, calcine solutions were prepared by adding calcine (100 mg) into buffer solution (500 mL, pH 9.18). Selective dying of the CaCO₃ with a fluorescent dye was performed by adding the calcine solution (20 mL), followed by flushing the cross-flow cell chamber with scale-forming solution (2.0 L). FM images were recorded every 12 h during 48 h. After 48 h of the scaling test, the membrane surface was further studied for 4 h using a 500 mL/min flow to monitor the possible scaling detachment. In all of the FM images of the membranes, the solution was fed from left to right. CaCO₃ on the membranes was imaged using blue light ($\lambda = 490$ nm). The camera used was a CMOS microscope digital eyepiece camera (MC500, Ostec, Guanzhou, China), acquiring images with an exposure time of 196 ms and equipped with an epifluorescence mode (SMZ18 stereomicroscope; Nikon, Tokyo) by a P2-EFLC green filter. The membrane was regenerated by acid wash using acetic acid (5.0 vol %) for 30 min at 21 ± 1 °C under 0.7 MPa and a flow rate of 500 mL/min. After the cleaning process, the scaling experiments were repeated for each membrane. Zeta potentials were measured using an electrokinetic analyzer (SurPASS3, Anton Paar, Graz, Austria) by the streaming potential technique. Two pieces of each membrane (1.0 × 2.0 cm) were fixed to the holders with waterproof double-sided tape and then set facing each other with a 110 µm space. KOH (0.05 mol/L) and HCl (0.05 mol/L) were used for the titration, and KCl (1.0 mmol/L) was used as an electrolyte solution.

MD Simulation. Classical MD simulations were performed using the LAMMPS code.48 Our target was to simulate the interaction of Ca²⁺ and CO₃²⁻ ions with the plain PA and G-PA composite hydrated models. The G-PA model represents the PA deposited on the outer surface of a large diameter-MWNT. This model takes into account the influence of the MWNT on the topology of the PA similar to our previous work31 and the charge transfer of the PA to the outer walls of the MWNT.49 The simulation on the diffusion of Ca²⁺ and CO₃²⁻ ions, as well as ACC, was performed using the flexible force-field parameters reported by Raiteri and Gale,25,26 considering the theoretical basis described in other studies.44,45 Additional details of the simulation are available in Supporting Information section S1.3.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00601.

Experimental methods; Experimental setup for FM, SEM and optical/fluorescence microscopy images; EDS mapping; and additional MD analyses (PDF)

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Y.T. and S.I. contributed equally to this work. Y.T. performed scaling experiments, FM observation, zeta potential measurement and SEM and wrote the manuscript draft. S.I. prepared the membranes and helped with scaling experiments. T.A., A.Y, and S.T. performed and analyzed the MD simulations. M.O. performed SEM and EDX. J.O.M., A.M.G, A.N., K.T., T.H., R.C.S., and M.T. advised and discussed the results during the project. M.E. proposed and supervised the project. All authors reviewed and approved the manuscript.

Notes
The authors declare no competing financial interest.

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