Electronic Supplementary Material

Self-healing polyamide reverse osmosis membranes with temperature-responsive intelligent nanocontainers for chlorine resistance

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Experimental Section

TFC and TFN membranes with different polymer nanocontainer additions were prepared and their water permeability and NaCl rejection were compared to determine the optimal addition of polymer nanocontainers in the polyamide layer. As shown in Figure S1, initial water permeability and NaCl rejection of the TFC membrane were 5.45 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ and 98.16%, respectively. With the increase of the amount of polymer nanocontainers, the water permeability and NaCl rejection of the membranes gradually increased, mainly because the surface of T-INC consists of hydrophilic PVA material, and partially exposed polymer nanocontainers could enhance the hydrophilicity of the membrane surface, which could attract many water molecules through the membrane and increase water permeability. In addition, polymer nanocontainers facilitate the formation of more abundant the "ridge and valley" structure on the membrane surface, the higher the surface area of the polyamide layer structure with separation performance,

and the higher the pathway for water molecules to pass through. On the other hand, if the number of T-INC continues to increase, it may cause the polyamide structure on the membrane surface to break down, and lots of water molecules would pass through the breakage, resulting in a decrease in NaCl rejection. The maximum water permeability and NaCl rejection of the membrane was achieved when the polymer nanocontainers were added at 0.0050 wt.%, especially the NaCl rejection reached 98.47%, which was 0.31% higher than that of the TFC membrane. Therefore, 0.0050 wt.% was determined as the optimum content of polymer nanocontainers in the polyamide membrane.

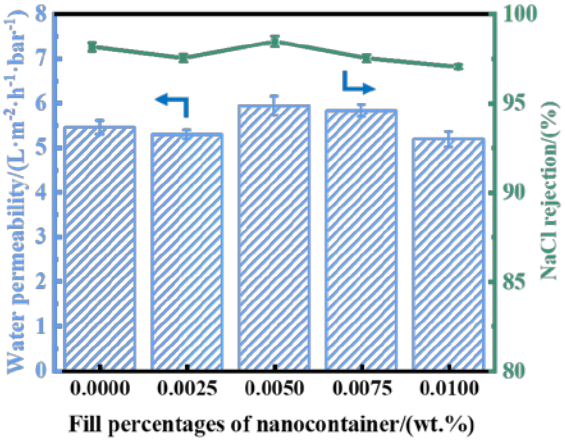

Figure S1. Water permeability and NaCl rejection of TFC (0 wt.% nanocontainer) and TFN membranes with different concentrations of polymer nanocontainers (0.0025 wt.%, 0.0050 wt.%, 0.0075 wt.%, and 0.0100 wt.%).

The water permeability and NaCl rejection of TFC and TFN membranes can be significantly affected after immersion in different concentrations of sodium hypochlorite solutions for 1 h under chlorinated acidic and alkaline environments (Figure S2). As shown in Figure S2a, at pH=4, the changes in NaCl rejection of TFC and TFN membranes did not exceed 0.51% with the increase of chlorination concentration, while the permeability decreased rapidly, and the TFN membrane exhibited higher water permeability compared to TFC membrane. At a chlorination concentration of 2000 ppm, the NaCl rejection of TFC and TFN membranes was slightly decreased to about 98%. There are two main reasons: (1) Under acidic chlorination conditions, the active chlorine is mainly Cl_2, which increases with chlorination concentration. At

low sodium hypochlorite concentration, the Cl_2 content is less, and part of it can attack the amide bond, change the N-H bond to N-Cl bond, which decrease the membrane surface hydrophilicity and the solubility of water molecules on the membrane surface and thereby lead to the decrease of water permeability [1]. However, TFN membranes contain T-INC with PVA as the shell, and PVA consists of hydrophilic -OH to increase water solubility of membrane surface and thereby increases water permeability [2]. (2) Chlorination breaks the hydrogen bonding of the polyamide layer and increases the free degree of the polyamide polymer chain. Under high-pressure operation, the polyamide layer undergoes a "compaction effect" with increased mass transfer resistance, and the reduction of NaCl rejection is not significant. At high chlorine concentrations, higher Cl_2 content allows for direct aromatic ring electrophilic substitution, which causes more damage to the polyamide layer and greater deformation of the polymer chain, leading to a decrease in NaCl rejection.

As shown in Figure S2b, at pH=9, the NaCl rejections of TFC and TFN membranes changed no more than 0.8% with sodium hypochlorite concentration below 1000 ppm, and the water permeability of TFN membrane was lower than that of TFC membrane, mainly because the nanocontainers in TFN membrane could increase the density of polyamide layer under alkaline conditions with low chlorine concentration, resulting in slightly lower water permeability. At high chlorine concentration of 2000 ppm, the NaCl rejection of both membranes decreased rapidly. Meanwhile, the water permeability increased with the increase of chlorination concentration, and the water permeability of TFN membrane increased faster compared to TFC membrane. There are two main reasons: (1) Under alkaline conditions, active chlorine component in the solution is mainly HClO, which is less active and often reacts with terminal amine group, so the chlorination degradation of the membrane is less, and there is a " compaction effect" under high pressure, so the NaCl rejection of TFC and TFN membranes is basically unchanged. However, T-INC is added to the TFN membrane, the surface area of polyamide layer increases, and the damaged area increases dramatically, resulting in a faster decrease in the NaCl rejection. (2) The polyamide membrane was soaked in alkaline sodium

hypochlorite solution, and the -COOH group on the surface was hydrolyzed, which increased the hydrophilicity of the membrane surface. As the chlorination concentration increases, the damage of the polyamide layer intensifies, leading to a gradual increase in water permeability [3]. Due to large damaged area of the polyamide layer of the TFN membrane and the presence of more hydrophilic T-INC, water permeability was higher than that of the TFC membrane when the chlorination concentration was higher. This suggests that chlorination at low concentrations under alkaline conditions has less loss of polyamide membrane performances and that chlorination should be added to alkaline environment when removing biological contamination from the membrane surface.

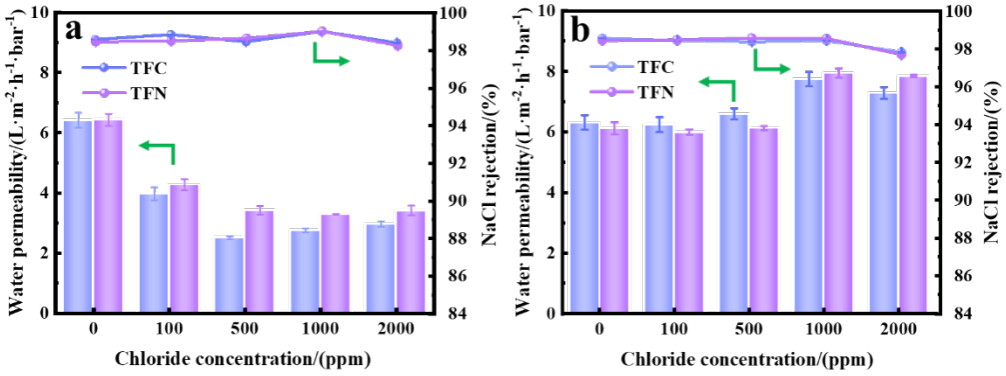

Figure S2. Performances of TFC and TFN membranes in solutions with different chlorination concentrations and different pH values: pH 4 (a) and pH 9 (b).

The TFC and TFN membranes before and after chlorination experiments were characterized by FTIR (Figure S3). Before chlorination (Figure S3a), the absorption peak at 1662 cm^{-1} is the stretching vibration of the C=O bond in the amide bond, the peak at 1610 cm^{-1} is the stretching vibration of the N-H bond, and the plane bending vibration of the N-H bond at 1540 cm^{-1}. Compared to unchlorinated polyamide membranes, the transmittances of TFC and TFN membranes treated with active chlorine increase to different degrees at the C=O and C-N bond, and the FTIR spectra changed significantly. After chlorination test at pH=4 (Figure S3b), the signal of the plane bending vibration of the N-H bond at 1540 cm^{-1} was weakened, and the signal disappeared or even merged into other absorption peaks; the absorption peak of the stretching

vibration of the C=O bond of the amide at 1662 cm^{-1} was blue-shifted to 1668 cm^{-1}; and the signal of the N-H bond at 1610 cm^{-1} disappeared. This indicates that chlorination leads to the destruction of original amide group, and some N-H bonds are converted to N-Cl bonds when chlorination is carried out at pH=4. Meanwhile, the N-H bonds lose their protons and cannot conclude hydrogen bonds. On the other hand, after chlorination at pH=9 (Figure S3c), the absorption peak of the stretching vibration of the C=O bond at 1662 cm^{-1} has not shifted significantly, and the peak intensities of the N-H bond at 1540 cm^{-1} and the plane bending vibrations of the C=O bond at 1610 cm^{-1} were also larger than those at pH=4. These phenomena suggest that the alkaline environment can significantly reduce the effect of chlorination on the membrane structure under the same chlorination conditions. In addition, at pH=9, the peak intensity of TFN membrane was less attenuated compared to TFC membrane, which was mainly attributed to the presence of T-INC in TFN membranes, where part of polymer nanocontainers acted as an intermediate layer to hinder the destruction of polyamide structure.

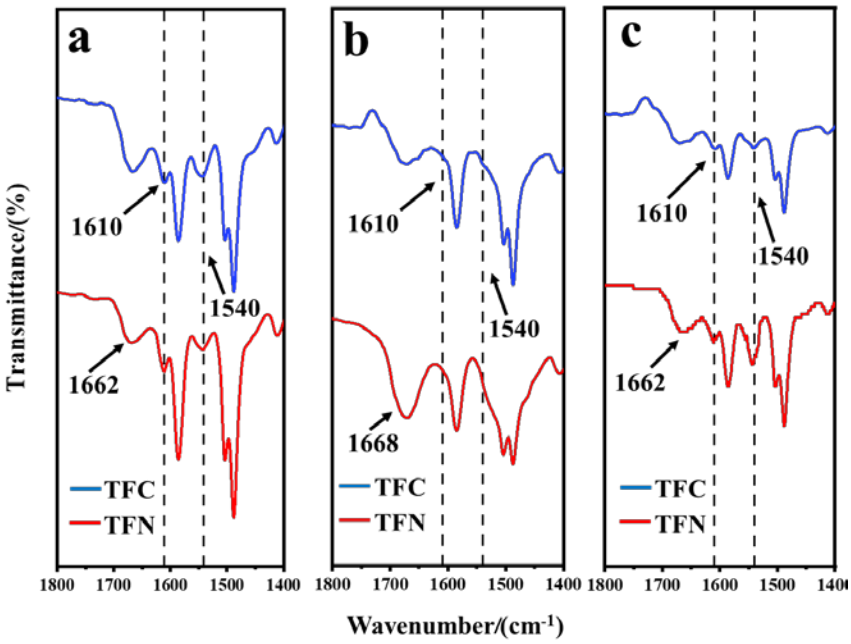

Figure S3. FTIR spectra of TFN and TFC membranes before (a) and after (b: pH=4; c: pH=9) chlorination tests.

References

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