Support Information

A hydrophobic-hydrophilic MXene/PVDF composite hollow fiber membrane with enhanced antifouling properties for seawater desalination

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Note S1: Mass transfer coefficient calculation

The total transfer coefficient k_{tot} can be calculated using the transfer equation [1]:

$$k_{\mathrm{tot}} = \frac{J}{\rho_{\mathrm{a}} \Delta\omega_{\mathrm{lm}}} \tag{1}$$

where J is the membrane permeate flux (kg/(m^2·h)); ρ_{a} is the air density (kg/m^3); and $\Delta\omega_{\mathrm{lm}}$ is the logarithmic mean humidity difference between the opposite sides of the membrane, which can be calculated by:

$$\Delta\omega_{\mathrm{lm}} = \frac{(\omega_{\mathrm{s}} - \omega_{\mathrm{a,i}}) - (\omega_{\mathrm{s}} - \omega_{\mathrm{a,o}})}{\ln(\omega_{\mathrm{s}} - \omega_{\mathrm{a,i}} / \omega_{\mathrm{s}} - \omega_{\mathrm{a,o}})} \tag{2}$$

where ω_{a} is the air humidity (kg moisture/kg air); the subscripts i and o represent the inlet and outlet, respectively (using the experimental data, $\omega_{\mathrm{a,i}}$= 0.00927 kg/kg and $\omega_{\mathrm{a,o}}$= 0.0119 kg/kg); and ω_{s} is the equilibrium humidity with the solution at a given liquid temperature and concentration (kg/kg), which can be calculated using Eq. (3):

$$\omega_{\mathrm{s}} = 0.622 \frac{P_{\mathrm{s},\nu}}{P_{\mathrm{atm}} - P_{\mathrm{s},\nu}} \tag{3}$$

where P_{atm} is the atmospheric pressure (101325 Pa) and $P_{\mathrm{s},\nu}$ is the water vapor partial pressure on the solution surface (Pa), which can be obtained from:

$$P_{\mathrm{s},\nu} = (1 - x_{\mathrm{s}}) P_{\nu} \gamma_{\mathrm{w}} \tag{4}$$

In Eq. (4), the activity coefficient of water (γ_w) can be obtained from the following empirical formula [2]:

$$\gamma_{\mathrm{w}} = 1 - 0.5 x_{\mathrm{s}} - 10 {x_{\mathrm{s}}}^2 \tag{5}$$

where x_{s} is the molality of the feed-side solution (mol NaCl/kg solution), which can be calculated using Eq. (6):

$$x_{\mathrm{s}} = \frac{m_{\mathrm{NaCl}} / M_{\mathrm{NaCl}}}{m_{\mathrm{NaCl}} / M_{\mathrm{NaCl}} + m_{\mathrm{w}} / M_{\mathrm{w}}} \tag{6}$$

where m_{NaCl} is the mass fraction of salt in the feed-side solution (3.5 wt% NaCl); M_{NaCl} is the molar mass of NaCl (58.5 g/mol); m_{w} is the mass fraction of water (96.5 wt% NaCl), and M_{w} is the molar mass of water (18 g/mol).

P_{ν} (Pa) is the water vapor pressure estimated by the Antoine equation at the feed temperature $T_{\mathrm{s,i}}$ as follows [2]:

$$P_{\nu} = \exp(23.238 - \frac{3841}{T_{\mathrm{s,i}} - 45}) \tag{7}$$

where $T_{s,i}$ is the temperature in Kelvin. This equation is valid in the temperature range of 273–373 K [3].

The resistance from the solution to the air side can be viewed as the sum of several resistances. The total mass transfer coefficient from the solution to the air (k_{tot}) was calculated based on the outer surface of the fiber, as described previously [4].

$$\frac{1}{k_{tot}} = \frac{1}{k_s^e}\left(\frac{d_o}{d_i}\right) + \frac{1}{k_m}\left(\frac{d_o}{\bar{d}}\right) + \frac{1}{k_a} \tag{8}$$

where k_m is the membrane mass transfer coefficient (m/s); k_a is the air mass transfer coefficient (m/s); and $\bar{d}$ is the arithmetic mean diameter of the fiber (m), $\bar{d} = 0.5 \times (d_o + d_i)$.

The mass transfer on the solution side was calculated as follows:

$$\rho_a k_s^e \Delta\omega_s = \rho_s k_s \Delta(1 - m_s) \tag{9}$$

where the equivalent mass transfer coefficient (k_s^e) based on the humidity difference is:

$$k_s^e = \frac{\rho_s}{\rho_a} k_s H_P \tag{10}$$

where H_P is the partition coefficient of the solution on the feed side, which is the slope of the water uptake in the solution to the equilibrium humidity:

$$H_P = \frac{\Delta(1-m_s)}{\Delta\omega_s} \tag{11}$$

where m_s represents the mass fraction of salt in the solution (kg NaCl/kg solution).

k_s is the solution mass transfer coefficient (m/s), which was calculated using the following series of equations [5]:

$$u_s = \frac{V_s}{\frac{\pi}{4} n_f d_i^2} \tag{12}$$

where V_s is the volume flow of the solution (m^3/s), n_f is the number of fibers in the module, d_i is the inner diameter of the fiber (m), and u_s is the velocity of the solution in the fiber (m/s).

$$Re_s = \frac{d_i u_s}{\nu_s} \tag{13}$$

where ν_s is the kinematic viscosity of the solution (m^2/s) and Re_s is the Reynolds number (Re_s=734, which is <2300, thus the flow in the membrane fiber tube was laminar).

The mass transfer inside the hollow fiber membrane was determined as described previously [6]:

$$Sh_s = 1.62\left(\frac{d_i^2 u_s^2}{L D_{ws}}\right)^{1/3} \tag{14}$$

$$k_s = \frac{Sh_s D_{ws}}{d_i} \tag{15}$$

where L is the length of the module (m), D_{ws} is the water diffusivity in solution (m^2/s), and Sh_s is the Sherwood number.

Similarly, the mass transfer coefficient of air (k_a) was calculated as follows:

$$\varphi = \frac{n_f d_o^2}{W \times H} \tag{16}$$

$$u_a = \frac{V_a}{L \times H} \tag{17}$$

where φ is the packing fraction, u_a is the velocity of the air (m/s), and V_a is the volume flow of the air (m^3/h).

When $P_D > (P_T + d_o)/2$, $u_{a,max}$ is:

$$u_{a,max} = \frac{P_T}{P_T - d_o} u_a \tag{18}$$

where P_D is the diagonal pitch (m), P_T is the transverse pitch (m) [7], and d_o is the outer diameter of the fiber (m).

$$Re_a = \frac{d_o u_{a,max}}{\nu_a} \tag{19}$$

where ν_a is the kinematic viscosity of the air (m^2/s), and the Reynolds number of the air side was calculated as 34.16 (<500).

Thus, the following correlations were used to calculate the Sherwood number [8]:

$$Sh_a = 0.15 Re_a^{0.8} Sc_a^{0.33} \tag{20}$$

$$Sc_a = \frac{\nu_a}{D_{va}} \tag{21}$$

$$k_a = \frac{Sh_a D_{va}}{d_o} \tag{22}$$

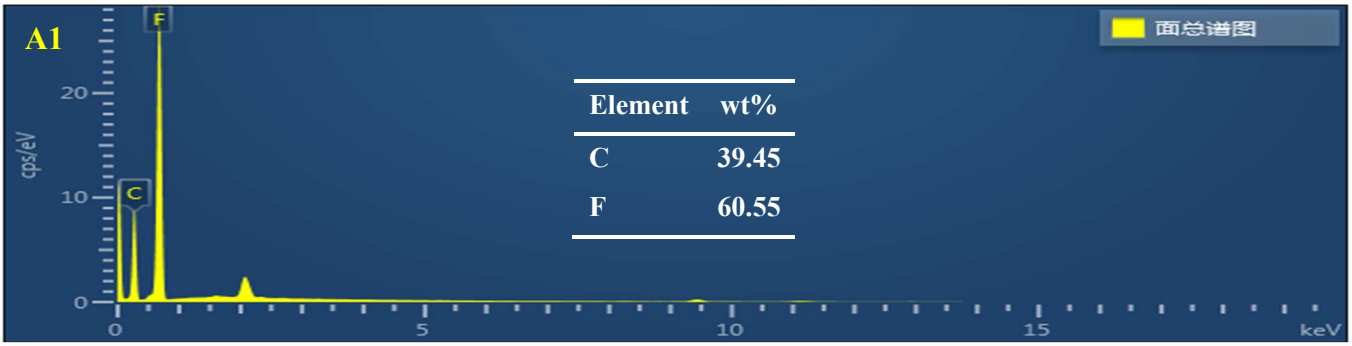
where Sc_a is the Schmidt number and D_{va} is the moisture diffusivity in the air (m^2/s). According to Eq. (8), the membrane mass transfer resistance can be calculated as follows:

$$\frac{1}{k_m} = \left(\frac{1}{k_{tot}} - \frac{1}{k_s^e}\left(\frac{d_o}{d_i}\right) - \frac{1}{k_a}\right)\frac{\bar{d}}{d_o} \tag{23}$$

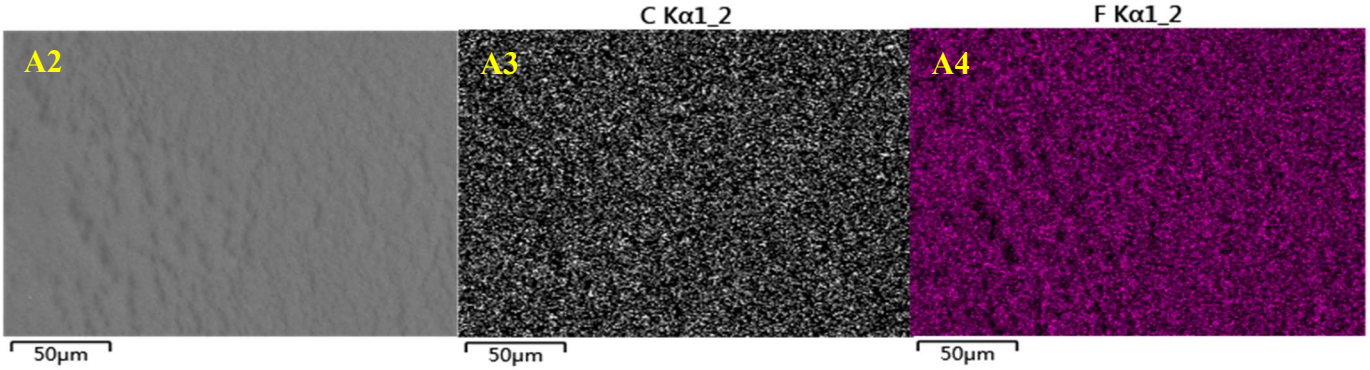
The moisture transfer resistance (s/m) of the composite membrane can be calculated from two layers:

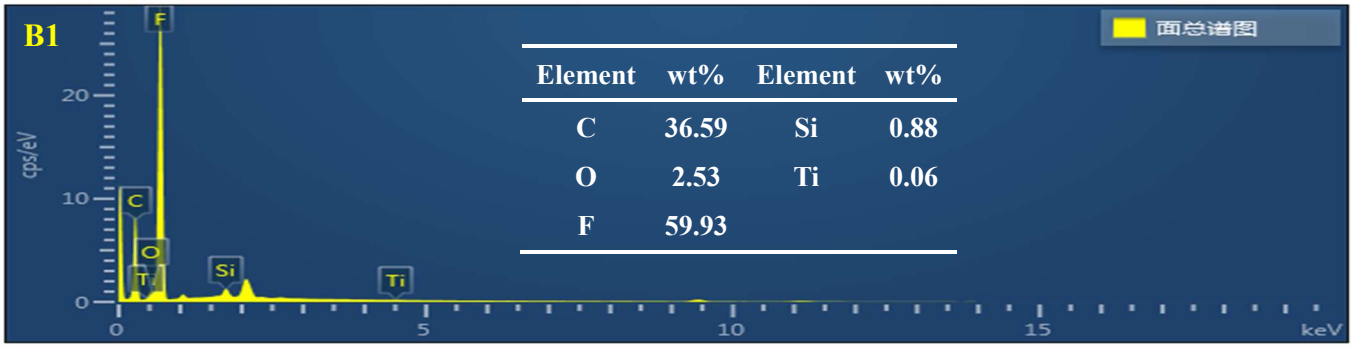
$$\frac{1}{k_m} = \frac{1}{k_{m1}} + \frac{1}{k_{m2}} \tag{24}$$

where m1 represents the PVDF hollow fiber membrane layer and m2 represents the MP layer in this study.



Element	wt%
C	39.45
F	60.55





Element	wt%	Element	wt%
C	36.59	Si	0.88
O	2.53	Ti	0.06
F	59.93		

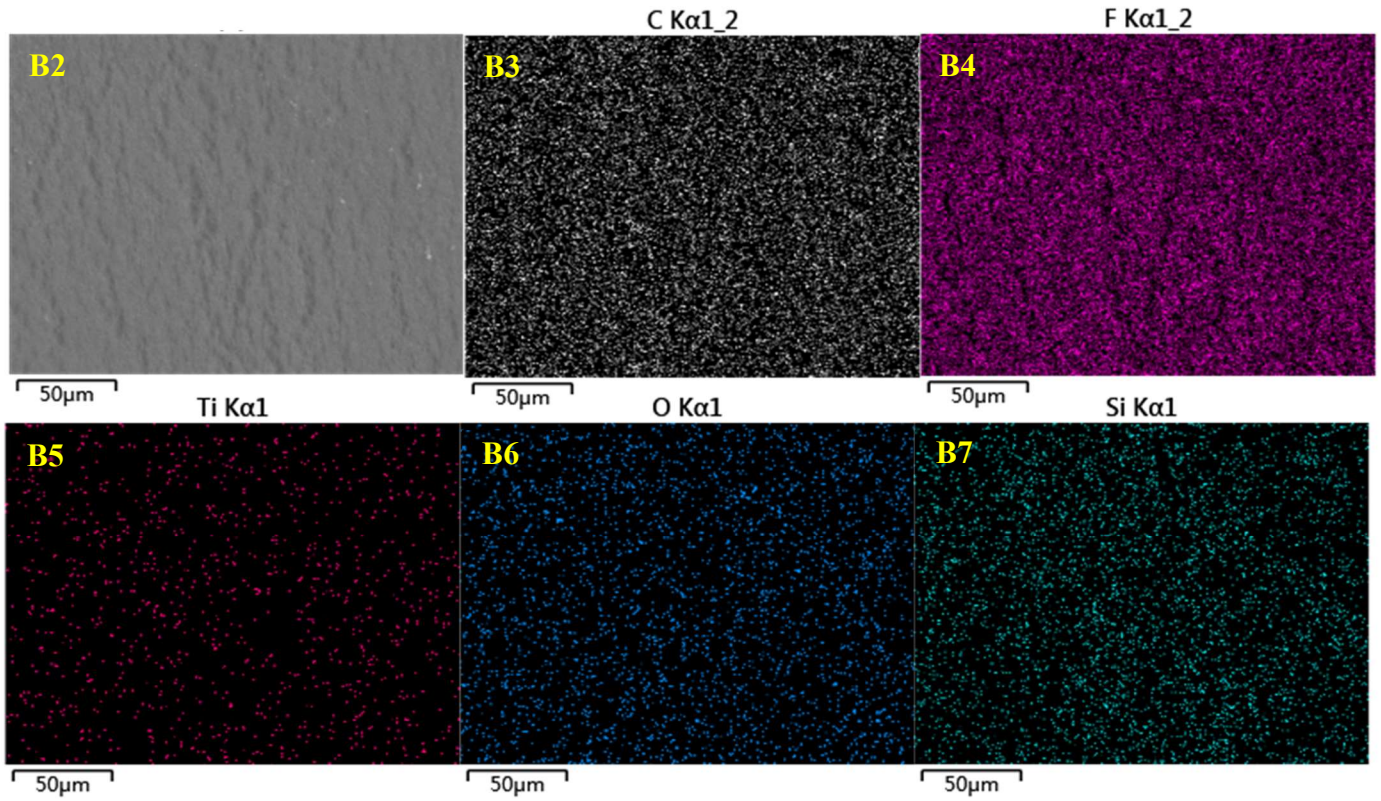


Fig. S1. Elemental composition and mapping results from the EDX analysis of the (A) PVDF hollow fiber membrane and (B) PVDF-MP hollow fiber membrane.

The elemental composition and mapping results from the EDX analysis of the PVDF and PVDF-MP hollow fiber membrane are shown in Fig. S1. Pure PVDF only contains C and F elements, while Ti, O, and Si were evenly distributed on the PVDF-MP membrane surface. The Ti was from MXene and O and Si were from PFDTMS, which demonstrated the successful grafting of the modified layer on the PVDF surface.

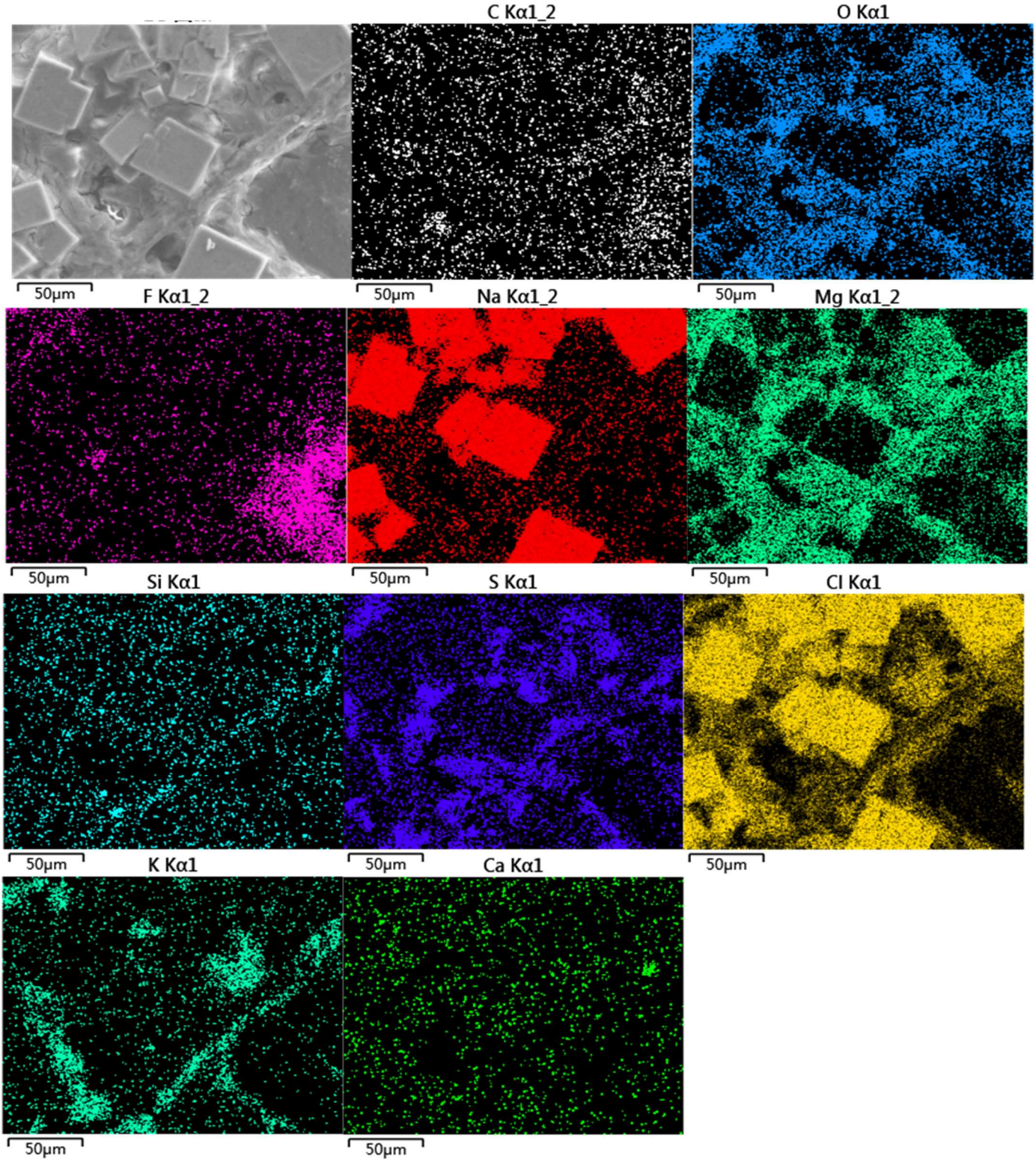


Fig. S2. EDX mapping results of the PVDF hollow fiber membrane after the test.

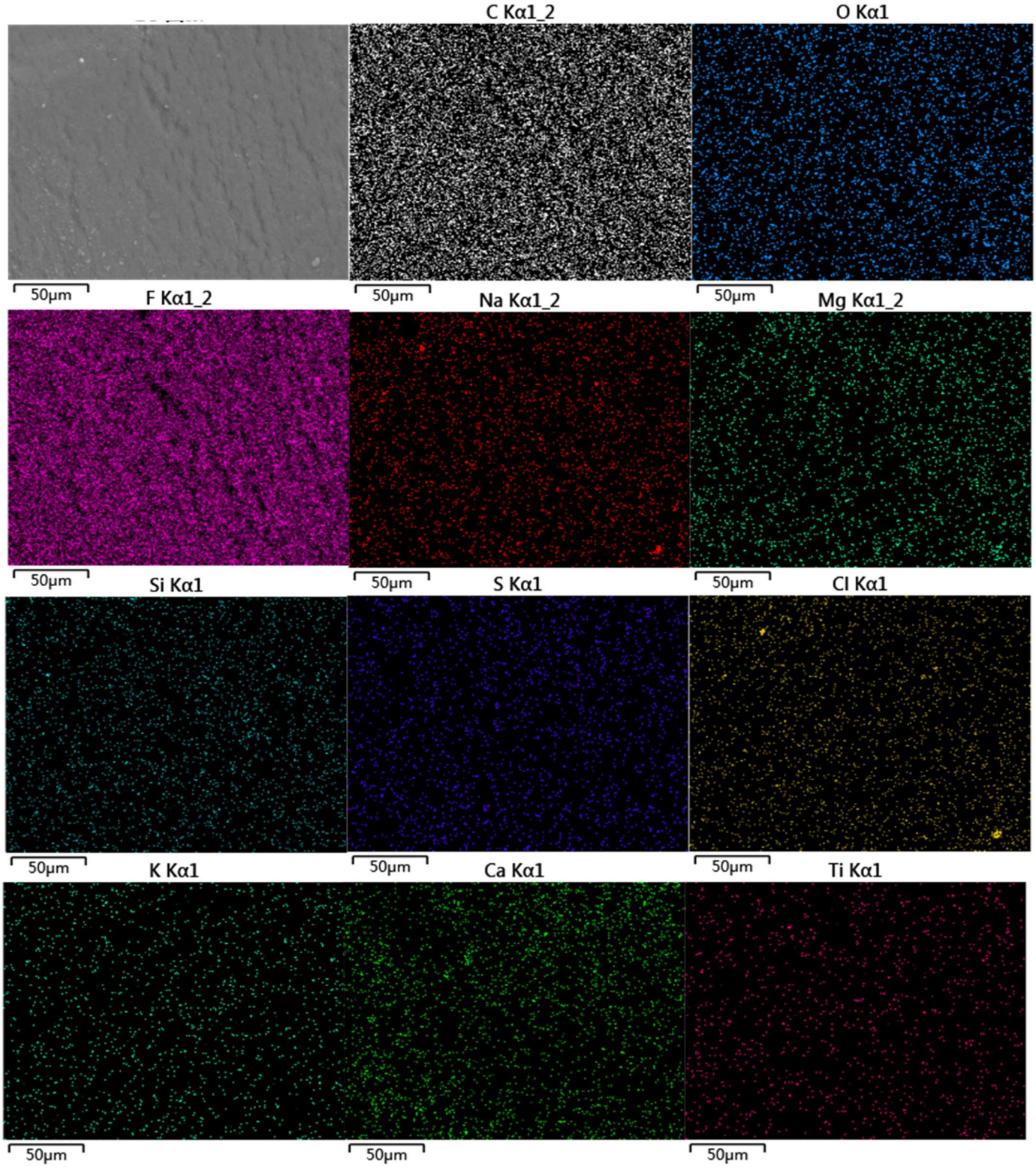


Fig. S3. EDX mapping results of the PVDF-MP hollow fiber membrane after the test.

The EDX mapping results of the inner surface of the PVDF and PVDF-MP membranes after 120-h seawater testing are displayed in Fig. S2 and S3. Compared to the pristine PVDF membrane (Fig. S1(A1–4)), many salt crystals (e.g., NaCl and KCl) and limescale (e.g., $MgSO_4$ and $MgCO_3$) covered the PVDF membrane surface after the test (Fig. S2). In contrast, few contaminants were observed on the PVDF-MP membrane

surface after the test, (Fig. S2), indicating that it had less fouling than the pure PVDF membrane.

Supplementary Reference

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