Transport Channel Regulated MXene Membrane via Organic Phosphonic Acids for Efficient Water Permeation

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Experimental section

Materials

All chemicals from chemical suppliers were used as received without any further purification. High purity (≥ 99%) Ti$_3$AlC$_2$ MAX phase powder (400 mesh) was purchased from Laizhou Kai Kai Ceramics Materials Co., Ltd. Hydrochloric acid (HCl, 37%) was supplied from VWR International. Dopamine hydrochloride, Tris (hydroxymethyl) aminomethane (THAM, ≥ 99.8%), Copper sulfate (CuSO$_4$, ≥ 99.99%), Lithium fluoride (LiF, ≥ 99.98% trace metals basis), Iminodi(methylphosphonic acid) (2P, 97%), Nitrilotri(methylphosphonic acid) (3P, ≥ 97%), phytic acid solution (PA, 50%), Diethylenetriaminepenta(methylphosphonic acid) solution (5P, 50%), Congo Red (CR, ≥ 35%), Eriochrome black T (BT, indicator grade), Methylene blue (MB, ≥ 97.0%), Rose Bengal (RB, 95%) were ordered from Sigma-Aldrich. Nylon-66 commercial microfiltration membrane was purchased from Tianjing JinTeng Experiment Equipment Co., Ltd. Deionized (DI) water was used throughout the experiment unless particularly stated.

Synthesis of MXene:

MXene dispersion was synthesized following the minimally intensive layer delamination (MILD) method as reported previously,\textsuperscript{1} with minor modification. In detail, 1.5 g high purity MAX powder (equivalent of 12 M) was cautiously added into the mixture of 30 mL 9 M HCl and 2.4 g LiF under continuously stirring over the course of 10 min (ice bath). The etching reaction was stirred and kept for 36 h at room temperature. Then the multilayer Ti$_3$AlC$_2$ and unetched MAX particles were washed and centrifuged (10000 rpm and one hour for each cycle) with DI water until the supernatant reached a pH value about 6. Ti$_3$C$_2$T$_x$ sheets suspension was produced by the exfoliation process of resultant slurry under ultrasonication for 1 h under the N$_2$ flow environment. The concentration of Ti$_3$C$_2$T$_x$ suspension was obtained by calculating the weight of dry Ti$_3$C$_2$T$_x$ sheets.

PDA coating of nylon-66 substrate:

Dopamine hydrochloride (2 mg/mL) was dissolved in an aqueous solution (pH = 8.5, mM) containing tris (hydroxymethyl) aminomethane (THAM) and CuSO$_4$ (5 mM). A nylon-66 substrate was immersed in the dopamine THAM buffer solution for 3 h at 40 °C. Subsequently, it was washed by DI water to remove the residual PDA solution and then stored in DI water prior to use.

Fabrication of OPA modified MXene membrane:

A certain amount of Ti$_3$C$_2$T$_x$ suspension was added into OPA solution dropwise with stirring for a certain time at room temperature. PA solution with the concentration varied from 0 – 4.0
wt% was applied for the concentration optimization of the modifier. The concentration of 2P, 3P and 5P solution was controlled as the equal molar ratio of PA solution. After the modification of OPA molecules, the resultant \( \text{Ti}_3 \text{C}_2 \text{T}_x \) suspensions were vacuum filtrated on PDA-coated nylon-66 supports to obtain the MXene membranes. [S1].

**Characterizations:**
The morphology of the membrane was characterized by scanning electron microscopy (SEM, JEOL 7000, Japan) operated at 5 kV, and the element distribution was detected with the energy dispersive X-ray spectroscopy (EDX) of SEM. The transmission electron microscopy (TEM, JEOL JEM-2100F, Japan) and selected area electron diffraction (SAED) studies were performed under an accelerating voltage of 100 kV. Atomic force microscopy (AFM, Veeco Instruments, CA) was conducted utilizing a Nanoscope V in tapping mode. Powder X-ray diffraction (PXRD, Bruker, D8 Advance, America) patterns of the membrane were collected using \( \text{Cu-K} \alpha \) radiation at 40 kV and 40 mA in the \( 2\theta \) angle range of 5° to 90°, with the scan step of 0.02°. Zeta potential and dynamic light scattering (DLS) measurements were performed on a Zetasizer (Malvern, England). X-ray photoelectron spectroscopy (XPS, Thermo Fisher, Escalab 250Xi, America) analysis was carried out using a monochromatic \( \text{Al-K} \alpha \) X-ray source \((h\nu = 1486.6 \text{ eV})\) operated at 150 W. Water contact angle (WCA) of the membrane surface was measured with a Geniometer (Krüss, DSA25, Germany) at ambient conditions.

**Nanofiltration (NF) performance tests of MXene membrane**
The separation performance of the membrane was evaluated using a lab-scale cross-flow NF filtration set up (Suzhou Faith & Hope Membrane Technology Co. Ltd.) with an effective area of 10.75 cm². Before testing, the membrane was pre-filtrated with DI water at 2 bar until the flux reached a steady state. The permeance was then collected under the operational pressure of 1 bar with the crossflow rate of 40 L/h. Various dye solutions (BT, CR, MB, RB) with the concentration of 100 ppm were employed as the feed solution for the tests. The permeability of the membrane was calculated using the following equation:

\[
\text{Permeability} = \frac{V}{A \times t \times P} \quad (1)
\]

where \( V \) is the permeate volume (L); \( A \) is the effective membrane area (m²); \( t \) is the filtration time (h). \( P \) is the operating pressure, fixed at 1 bar.

The dye rejection (R) was calculated as the following equation:

\[
\text{Rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)
\]
where $C_f$ and $C_p$ are the dye concentrations in the feed and permeate, respectively. The concentration was measured by a UV-Vis spectrophotometer (Thermo Fisher, GENESYS 150, America).

**Fig. S1.** EDS mapping of pure Ti$_3$C$_2$T$_x$ nanosheets membrane.

**Fig. S2.** XRD patterns of bulk Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$ nanosheets.
Fig. S3. HRTEM image (inset shows the SAED patterns) of Ti$_3$C$_2$T$_x$ nanosheets.

Fig. S4. DLS results of pure and OPA modified Ti$_3$C$_2$T$_x$ nanosheets suspensions.
Fig. S5. Zeta potentials of pure and OPA modified Ti$_3$C$_2$T$_x$ nanosheets suspensions.

Fig. S6. The digital photos of pure and OPA modified Ti$_3$C$_2$T$_x$ nanosheets suspensions after 12-h reaction.
Fig. S7. SEM images and mapping of (a) pure, (b) 2P/MXene, (c) 3P/MXene, and (d) 5P/MXene membrane. Inset shows the digital photo of the corresponding membrane on nylon-66 support.

Fig. S8. Cross-sectional SEM images of (a) pure, (b) 2P/MXene, (c) 3P/MXene, and (d) 5P/MXene membranes.
Figure S9. FT-IR spectra of pure and PA/MXene power.

Fig. S10. Peak deconvolution of narrow-scan spectra of O 1s for (a) 2P/MXene, (b) 3P/MXene, and (c) 5P/MXene membranes.

Fig. S11. The cross-sectional EDS mapping of (a) pure and (b) OPA modified MXene membranes.
Fig. S12. The effect of MXene loading on the separation performance of the MXene membrane.

Fig. 13. The digital photos of Ti$_3$C$_2$Tx nanosheets suspensions mixed with different amount of PA. (a) Just mixed, (b) after 12-h reaction.

Fig. S14. Separation performance of pure and OPA modified MXene membrane for (a) BT, (b) MB and (c) RB. (Feed concentration: 100 ppm, operational pressure: 1 bar, crossflow rate: 40 L/h)
Fig. S15. Water contact angles of the pure and OPA modified MXene membranes.

![Bar chart showing water contact angles for different membranes](image)

Fig. S16. XRD patterns of pure and PA/MXene membranes before and after 10-cycle of testing.

![XRD patterns](image)

Table S1. Surface elemental composition of the pure and OPA modified MXene membranes by XPS analysis.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>C 1s</th>
<th>O 1s</th>
<th>F 1s</th>
<th>Ti 2p</th>
<th>P 2p</th>
</tr>
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<tr>
<td>Mxene</td>
<td>45.37</td>
<td>17.24</td>
<td>12.16</td>
<td>25.22</td>
<td>/</td>
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<tr>
<td>2P/Mxene</td>
<td>41.59</td>
<td>22.62</td>
<td>9.88</td>
<td>24.16</td>
<td>1.76</td>
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Table S2. Surface elemental composition of the pure and OPA modified MXene membranes by EDS analysis.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Atomic percentage (%)</th>
<th>C K</th>
<th>O K</th>
<th>F K</th>
<th>Ti K</th>
<th>P K</th>
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<tr>
<td>Mxene</td>
<td>41.74</td>
<td>32.33</td>
<td>25.92</td>
<td>0.01</td>
<td>/</td>
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<td>2P/Mxene</td>
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<td>39.28</td>
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<td>1.93</td>
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<td>3P/Mxene</td>
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<td>5P/Mxene</td>
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<td>5.96</td>
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<tr>
<td>PA/Mxene</td>
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<td>0</td>
<td>2.11</td>
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Note: The signal of Ti element was overlapped with that of O, thus zero atomic percentage of Ti.

Table S3. Benchmarking of MXene membranes for dyes nanofiltration.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Operational pressure (bar)</th>
<th>Permeance (L/m² h bar)</th>
<th>Dye rejection (%)</th>
<th>Molecular weight (g/mol)</th>
<th>Feed conc. (mg/L)</th>
<th>Ref.</th>
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<tr>
<td>RGO/PDA/MXene</td>
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<td>95</td>
<td>319.9</td>
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<td>²</td>
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<td>28.94</td>
<td>94.7</td>
<td>319.9</td>
<td>75</td>
<td>³</td>
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<tr>
<td>Mxene</td>
<td>1</td>
<td>340.5</td>
<td>95.1</td>
<td>514.4</td>
<td>100</td>
<td>⁴</td>
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<tr>
<td>Crumpled Mxene</td>
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<td>357</td>
<td>67.7</td>
<td>960.8</td>
<td>20</td>
<td>⁵</td>
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<tr>
<td>GO/Mxene</td>
<td>5</td>
<td>16.7</td>
<td>98.6</td>
<td>319.9</td>
<td>10</td>
<td>⁶</td>
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<tr>
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<td>96.3</td>
<td>1111.1</td>
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<td>90</td>
<td>960.8</td>
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<tr>
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<td>514.5</td>
<td>99.6</td>
<td>696.7</td>
<td>100</td>
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</tr>
<tr>
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<td>98.3</td>
<td>416.4</td>
<td>100</td>
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References


