Supporting Information

Two-dimensional Ti$_3$C$_2$Tx MXene Membranes as Nanofluidic Osmotic Power Generators

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1. Exfoliation of MXene Ti$_3$C$_2$Tx and its morphology

**Figure S1** (a) Selective aluminum layer etching process by in-situ HF-forming etchant: exfoliation of individual Ti$_3$C$_2$Tx nanosheet from MAX phase Ti$_3$AlC$_2$ precursor.\(^1-^4\) (b) topological map of single layer Ti$_3$C$_2$Tx nanosheets deposited on a Si/SiO$_2$ substrate, investigated by AFM (Scale bar: 2 μm).\(^1, 5\) To determine the thickness of a single nanosheet, a sheet-to-sheet procedure from overlapped region is used to exclude instrumental artifacts or the influence of possible contaminants on substrates.\(^6\)

2. Thickness control of MXene lamellar membranes

**Figure S2** Membrane thickness *versus* loading amount of Ti$_3$C$_2$Tx flakes. The thickness of filtrated films can be precisely controlled by adjusting the loading amount of MXene Ti$_3$C$_2$Tx nanosheets. Inset shows the cross-section SEM image of the lamellar membrane.
3. XPS analysis of MXene Ti$_3$C$_2$T$_x$ membranes

Figure S3| Curve fitted spectrum for regions of (a) Ti2p, (b) C1s, (c) O1s and (d) F1s, obtained from stacked Ti$_3$C$_2$T$_x$ membranes. The survey spectra show four possible moieties of surface termination existing on Ti$_3$C$_2$T$_x$ lamellar membranes: C-Ti-O, C-Ti-(OH)$_x$, C-Ti-F$_x$, and Ti$_3$C$_2$OH-H$_2$O. Ti-C and Ti-O bonds confirm the formation of Ti$_3$C$_2$T$_x$ with oxygen containing termination after the Al etching process. 7-10
4. Determination of nanocapillaries dimensions and surface porosity

The stacked Ti₃C₂Tx sheets in the layered structure are separated by an interlayer distance \(d\) \(\sim\) 16.2 Å in fully hydrated state. Taking into account that a theoretical thickness \(a\) of monolayer Ti₃C₂Tx sheet is \(\sim 9.8\) Å, the empty space, which is available for ions to diffuse, is estimated to \(\delta = (d - a) \sim 6.4\) Å. This effective interplanar spacing for ion transport is corresponding to the height of a nanocapillary.

As shown in Figure S4, a full length of a single nanocapillary with thickness \(h\) involves a number of turns \(h/d\), and each turn involves a capillary length \(w\). Here, we assumed that the single Ti₃C₂Tx sheet possesses same width and length, and those are approximated from experimentally averaged lateral sizes \((\approx 3.4\ \mu\text{m})\) of the MXene sheets. Therefore, the complete length of single nanocapillary is given by \(w \times h/d\). The total number of parallel 2D channels per unit area can be estimated as by \(1/w^2\), and a resulting number of channels is \(\sim 10^7\) across an employed membranes with a full area of 0.196 cm². The effective areal fraction of the nanocapillaries on total membrane area is estimated to be approximately 0.1 %, in well agreement with previously reported results.¹¹

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**Figure S4** | Dimensions of a confined nanocapillary across the lamellar MXene membrane
5. Effect of pH on surface zeta potentials and the interlayer spacing of membranes

Figure S5 | (a) Surface zeta potentials and (b) XRD spectra and of fully hydrated Ti₃C₂Tx lamellar membranes at different pH values. The pH-dependent protonation/deprotonation of the charged functionalities are obviously identified from the surface zeta potentials of the hydrated membranes. In addition, the interplanar channel height shows a strong dependency on pH. More specifically, lower pH exhibits limited hydration behavior in the fully wet membranes, due to weakened repulsive force between protonated surface functional groups. ¹², ¹³

6. Electroosmotic flow through non-ion selective support membrane

Figure S6 | Electroosmotic transport behavior through bare hydrophilic PTFE membranes under KCl concentration gradient of 100. The PTFE support membrane yields weak opposite charge-driven (or non-selective) transport behavior, contrasting to the Ti₃C₂Tx film showing the strong cation-selective transport behavior. Furthermore, higher conductance of the support PTFE, measured in linear regime at smaller biases (< 30 mV), confirms clearly that the deposited Ti₃C₂Tx membrane determines the osmotic power performances under concentration gradient.
7. Electrode calibration

According to the equivalent circuit diagram in the power generation system (Inset of Figure 3a), the osmotic potential across membranes can be corrected as follows

\[ V_{os} = V_{oc} - V_{\text{redox}} \]

The \( V_{\text{redox}} \) is the redox potential arising from unequal chloride concentration at a pair of electrodes. Especially, taking into account a temperature-dependent activity coefficient, the redox potential can be calculated by the Nernst equation in combination with the Pitzer model.

\[
V_{\text{redox}}(T) = \frac{RT}{zF} \ln \frac{\gamma_{CH}(T)c_H}{\gamma_{CL}(T)c_L}
\]

where \( R \), \( z \), and \( F \) are the gas constant, charge valence, and Faraday constant, respectively. The \( \gamma(T) \) is the temperature-dependent activity coefficient described by the Pitzer model. \(^{12-18}\) For the electrode correction, experimentally estimated redox potential as plotted in Figure S7 is used at elevated temperature.\(^ {19}\)

**Figure S7** | Linear plot of experimental redox potential as a function of temperature, estimated at different KCl concentration gradients.\(^ {19}\)
8. Salt concentration gradient-dependent transference number

Figure S8| Cation transference number as functions of KCl concentration gradient and pH.

9. Membrane resistance versus osmotic power density

Figure S9| (a) Area membrane resistances of variable 2D lamellar membranes (Ti₃C₂Tx, C₃N₄, GO, and Kaolinite) with different thicknesses. The ionic conductances across each 2D system and commercially available cation exchange membranes (CEMs) are evaluated, respectively, with KCl 0.5 M, and NaCl 0.5 M. (b) Osmotic output power density over thickness.
10. Membrane thickness-dependent power generation

**Figure S10** Osmotic current and potential at different thicknesses under KCl concentration gradient of 1 M to 10 mM at pH 5.7.

11. Chemical stability

**Figure S11** Chemical stability of hydrated membranes, investigated after ionic transport at 55°C for 1 hr. The XRD spectrum after thermal stress is nearly identical to that from the fully hydrated membrane at ambient temperature, confirming that its chemical stability even at high temperature.
12. Performance stability

Figure S12| Time series of the osmotic current and potential under concentration gradient of 1 M to 10 mM at pH 5.7, measured at room temperature. The energy conversion performance of the MXene membranes was maintained within ± 8 % of averaged output power over 20 hours, showing their structural and chemical stability in aqueous solution.

13. Ionic species-dependent electroosmotic performances

Figure S13| Comparison of osmotic current and potential between KCl and NaCl, measured at elevated (a) salt concentration gradient and (b) temperature. (c) XRD spectra comparison between the fully hydrated and following air-dried membranes. The MXene membranes fully hydrated in water, KCl 1M and NaCl 1M display comparable swelling behaviors, and additionally no ion intercalation is revealed from both species even after air-drying process, evidenced by unaffected diffraction peaks.
### 14. Performance comparison of osmotic power generators

<table>
<thead>
<tr>
<th>No.</th>
<th>Materials</th>
<th>Thickness/Length (nm)</th>
<th>Concentration gradient: ( c_{\text{high}}/c_{\text{low}} )</th>
<th>Power Density ( (\text{W} \cdot \text{m}^{-2}) )</th>
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<tr>
<td>1</td>
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<td>0.18</td>
</tr>
</tbody>
</table>

*Table S1* | Performances of state-of-the-art micro- and nanoscale osmotic power generators
Supporting references


