Supplementary Information

Understanding the Swelling Behavior of $Ti_3C_2T_x$ MXene Membranes in Aqueous Media

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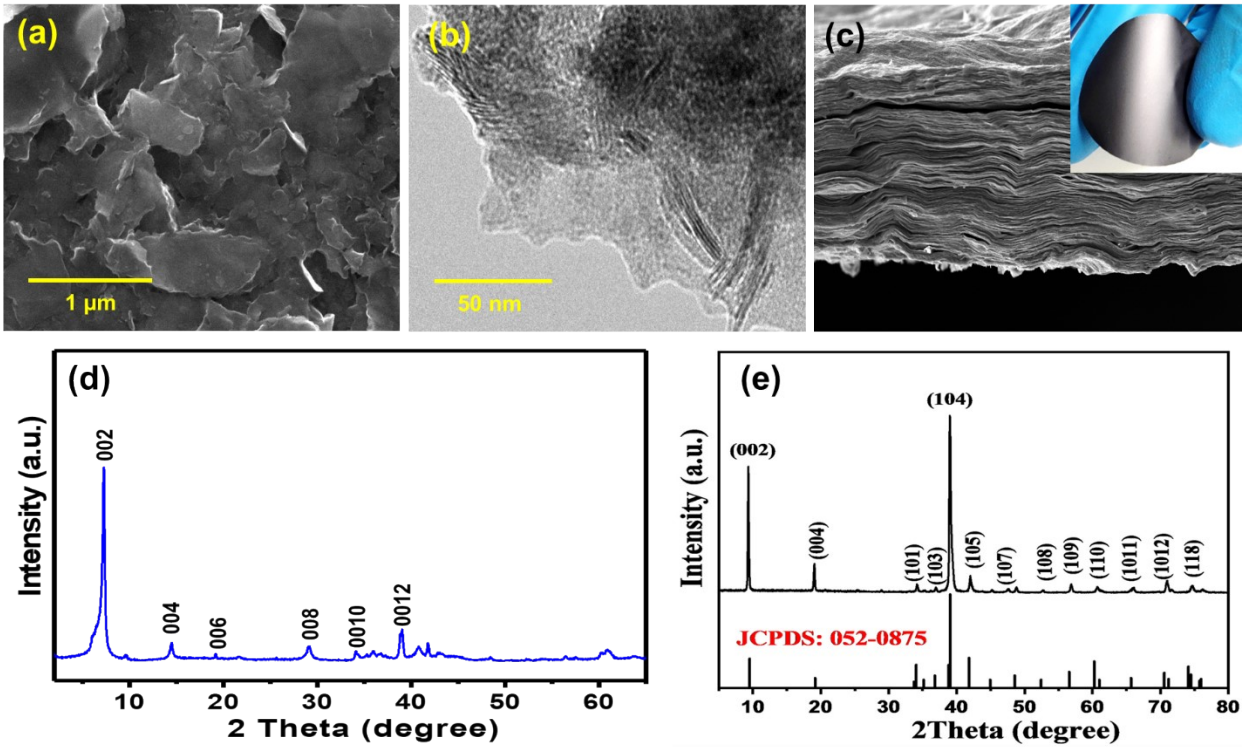

Figure S1: (a) SEM image of DL-$Ti_3C_2T_x$, (b) TEM image of DL-$Ti_3C_2T_x$, (c) Cross-section SEM image of DL-$Ti_3C_2T_x$ membrane (inset: an optical image of prepared DL-$Ti_3C_2T_x$, membrane) and (d) XRD pattern of DL-$Ti_3C_2T_x$, (e) XRD pattern of Ti_3AlC_2 MAX (reproduced with permission from Ref [1] .

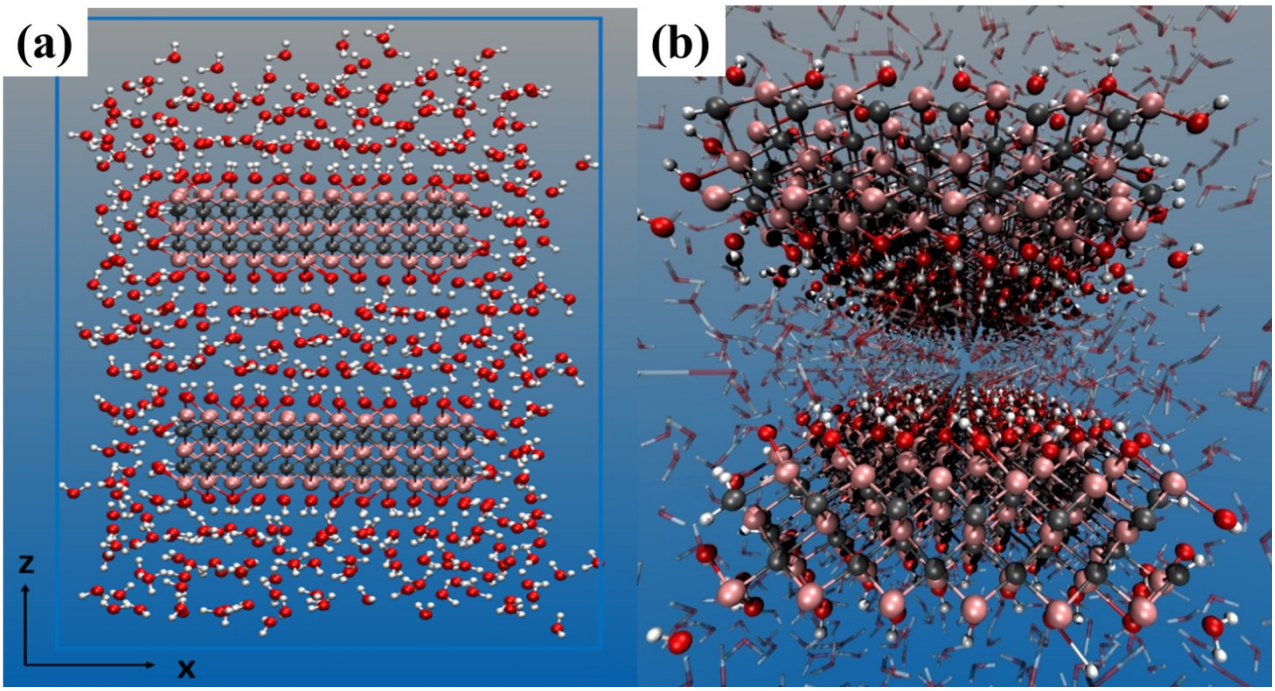

Figure S2: Initial configuration for the FPMD trajectory. Panel a) shows an orthographic view with the Y-axis perpendicular to the page. The simulation box is periodic in all three directions, which results in a 2D channel between two MXene layers and water can flow along the X-direction. Panel b) shows a perspective of Panel a): for visualization purposes, the periodic image along the Y-direction was duplicate in panel b). Color code: O(red), H(white), C(grey), Ti (pink).

XPS Experimental Analysis

Ti2p, O1s, C1s, and F1s XPS spectra of the four different cation intercalated samples are reported in Figure S3. Spectra baselines have been subtracted for better comparison without any normalization. As indicated in Figure S3 (left panel), the samples before etching show considerable variation in the T2p, O1s, and C1s spectra, which is expected due to the different surface termination groups. After imposing a sufficient Ar+ etching of the surface, the resulting XPS spectra show almost identical patterns for all the studied membranes. In particular, C1s shows various components C-Ti, C-C/C=C, C-O and C=O before etching for all samples. While after etching, the C=O. C-C disappeared with only a major C-Ti peak. This reflects the high purity of the inner Ti3C2Tx sheets that are not affected by the type of intercalated ions. The deconvolution of the main components after etching is presented in Figure S4. Binding energy positions of different components have been widely reported, and our results turned out to be in accordance with their values [2], which reveals several aspects: 1) Ti2p give mainly the Ti-C structure with the different Tix+ components; while 19% of the Ti should be assigned to the TiO_2 components; 2) several surface functional groups are attached to the sheet surface, including the -OH, the -O and fluoride(-F) species, some C=C related species seem to exist as well. The oxidation could have happened as the samples were characterized by XPS after storing them for 30 days under argon atmosphere.

We further evaluate the cation intercalation by looking at the corresponding ion core levels Na1s Al2p and Ca2p, as function of etching. A summary of their atomic concentration is list in Table S1 both before and after the Ar^+ etching process. The values for Ca^{2+} and Al^{3+} are obtained by calculating the areas from the high-resolution spectra of each element after a proper Shirley background subtraction, while the Na^+ case is obtained by a proper fitting procedure as the Na1s

signal is overlapping with the Ti-O2 and Ti-C LMM Auger features. Quantitatively, the pristine samples contain 3.18%, 2.46 and 1.37% of the Na^{+}, Ca^{2+}, and Al^{3+}, respectively. A sufficient etching time significantly reduces the cations values to 2.9%, 0.74%, and 0.96%, respectively.

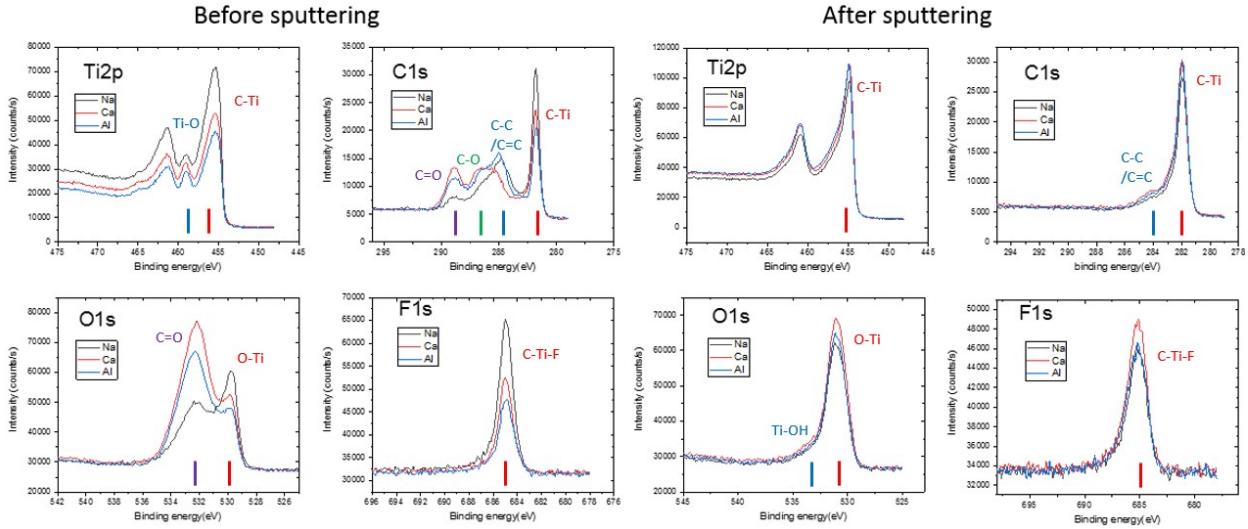

Figure S3: Comparison of the Ti2p, C1s, O1s, and F1s core level XPS spectra for the pre-etching samples (left panel) and the after-sputtering samples (right panel), for Na-MXene (gray), Ca-MXene (red), and Al-MXene (blue) membranes.

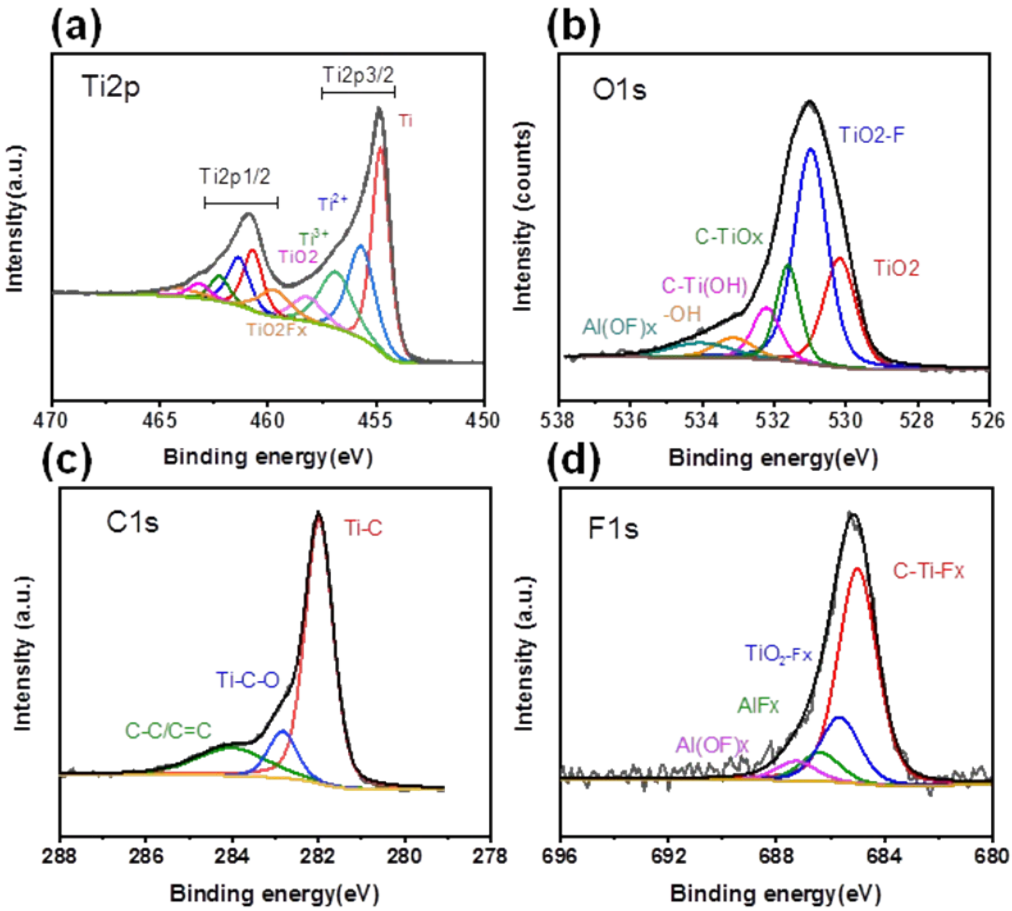

Figure S4: Fitting of the typical XPS Ti2p, C1s, O1s, and F1s spectra for MXene sample after etching.

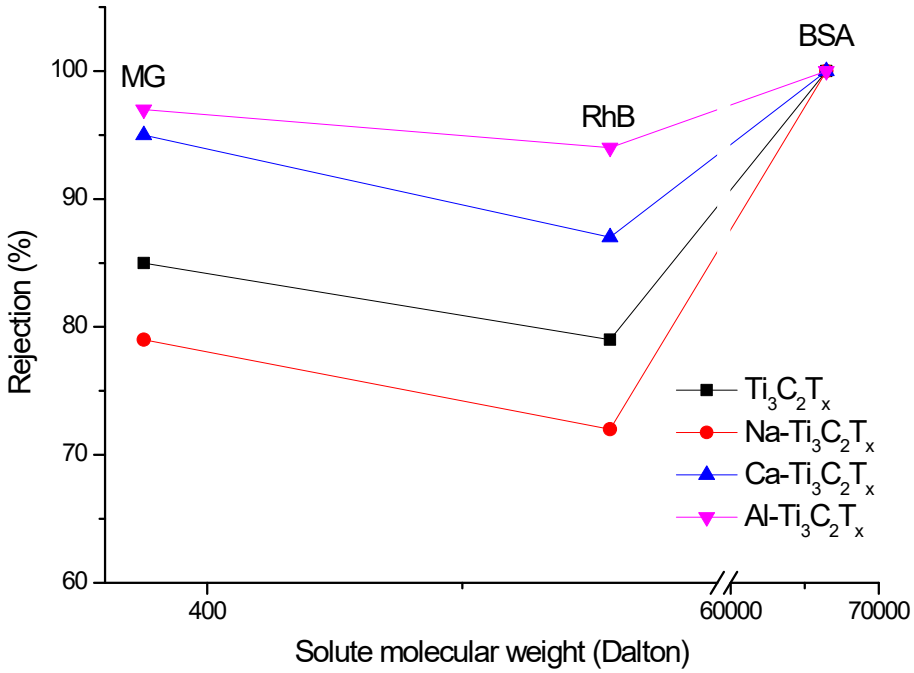

Figure S5: MWCO for pristine and Ion intercalated MXene membranes.

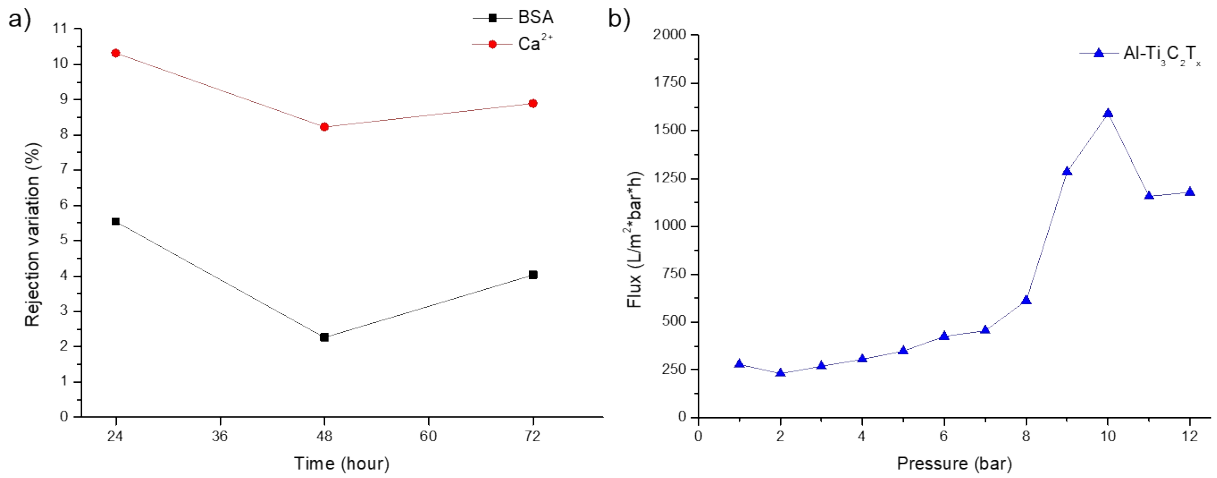

Figure S6: a) long-term stability; and b) water flux at different pressures for Al-MXene membrane.

Table S1: Atomic percentages based on the high-resolution XPS spectra, before and after the etching.

	Ti	C	O	F	Cl	Ca	Na	Li	Al
$Ti_3C_2T_x$ before	18.57	30.96	35.64	5.49	0.81	--	--	7.35	--
$Ti_3C_2T_x$ after	34.43	14.02	35.53	6.09	0.6	--	--	6.13	--
Na-$Ti_3C_2T_x$ before	25.93	34.93	24.07	9.62	2.27	--	3.18	--	--
Na-$Ti_3C_2T_x$ Xene after	40.14	23.61	23.42	8.19	1.74	--	2.9	--	--
Ca-$Ti_3C_2T_x$ before	17.85	35.57	35.53	5.61	1.72	2.46	--	--	--
Ca-$Ti_3C_2T_x$ after	39.38	23.77	25.57	6.31	1.55	0.74	--	--	--
Al-$Ti_3C_2T_x$ before	17.16	39.79	33.16	5.48	1.81	--	--	--	1.37
Al-$Ti_3C_2T_x$ after	39.3	23.68	24.83	6.5	1.5	--	--	--	0.96

Table S2: Thickness values for all the reported $Ti_3C_2T_x$ membranes calculated by *in-situ* ESEM between 40% and 90% RH.

	Membrane cross-section thickness (µm)			
	$Ti_3C_2T_x$	Na-$Ti_3C_2T_x$	Ca-$Ti_3C_2T_x$	Al-$Ti_3C_2T_x$
40% RH	20.88	26.87	2.915	5.47
90% RH	22.93	30.54	3.167	5.706
Increase Percentage	9.82%	13.66%	8.64%	4.31%

Table S3: Thickness values for all the reported $Ti_3C_2T_x$ membranes calculated by *in-situ* ESEM from 50°C to 300°C.

Degree °C	**Membrane cross-section thickness (µm)**			
	$Ti_3C_2T_x$	Na-$Ti_3C_2T_x$	Ca-$Ti_3C_2T_x$	Al-$Ti_3C_2T_x$
50	17.10	19.59	31.24	4.489
100	16.19	18.94	30.59	4.392
150	15.54	18.67	29.89	4.176
200	14.57	18.46	29.41	3.874
250	14.19	18.35	29.14	3.82
300	14.35	18.78	29.03	3.702
decrease percentage	-16.08%	-4.13%	-7.07%	-17.53%

Table S4: Hydration enthalpy values for the studied cations.[3]

Cation	Hydration enthalpy $-H°_{hyd}$ (kJ/mol)
Li^{+}	519
Na^{+}	409
Ca^{2+}	1577
Al^{3+}	4665

Table S5: Thickness values for all the reported $Ti_3C_2T_x$ membranes calculated by *in-situ* XRD, from 50°C to 300°C.

Degree °C	Membrane cross-section thickness (µm)			
	$Ti_3C_2T_x$	Na-$Ti_3C_2T_x$	Ca-$Ti_3C_2T_x$	Al-$Ti_3C_2T_x$
50	11.91	12.55	12.51	13.01
100	11.49	11.25	11.44	11.59
150	11.33	10.93	10.96	11.44
200	11.19	10.79	10.68	11.18
250	11.01	10.66	10.69	10.94
300	10.89	10.70	10.44	10.72
Decrease percentage	-8.56%	-14.74%	-16.54%	-17.60%

Table S6:

MXene-based membranes	Synthesis method	Ions	Ions concentration (mg/L)	Setup (dead-end/cross-flow)	Operating pressure (bar)	Water Flux (L/m²•h•bar)	Rejection (%)	Ref
PEI modified GO/MXene composite membrane (GO/MXene mass ratio = 1:4)	Vacuum filtration	Ca^{2+}	0.01M	Dead-end filtration system	1-4	1.3 ± 0.2–9.5 ± 0.4	73	4
		Mg^{2+}					78	
		Na^{+}					55	
		K^{+}					45	
2D cross-linked MXene ($Ti_3C_2T_x$)/ GO composite membrane	Vacuum-assisted filtration	Na^{+}	0.2M	u-shape	n/a	n/a	99.3	5
PFDTMS-modified hydrophobic 2D d-Ti_3C_2 membrane	Vacuum filtration	Cu^{2+}					~100	6
$Ti_3C_2T_x$-CNT hybrid membrane	Vacuum filtration	Au^{3+}	20	Vacuum filtration	1	437	99.8	7
$Ti_3C_2T_x$ membranes (Al^{3+}-intercalated MXMs)	Simple filtration and ion intercalating methods	NaCl	0.1M	u-shape		2.81	96.5	8
Micrometer thick $Ti_3C_2T_x$ membranes	Vacuum assisted filtration	NaCl	0.1 M	u-shape	4.89	37.4	55 (Pristine), 98 (SCMM-180)	9
		$MgCl_2$						
		$AlCl_3$						
GO/$Ti_3C_2T_x$	Vacuum filtration	Ca^{2+}	0.01M	dead-end	3	9.5	70	4

− PEI								
		Mg^{2+}	0.01M				80	
Ti3C2Tx membrane (Na^+ intercalated)	Vacuum filtration	Na^+	50	dead-end	1	377	9	this work
		Ca^{2+}					20	
		Al3+					30	
$Ti_3C_2T_x$ membrane (Ca^{2+} intercalated)	Vacuum filtration	Na^+	50	dead-end	1	294	12	this work
		Ca^{2+}					41	
		Al^{3+}					49	
$Ti_3C_2T_x$ membrane (Al^{3+} intercalated)	Vacuum filtration	Na^+	50	dead-end	1	279	14	this work
		Ca^{2+}					59	
		Al^{3+}					70	

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