

Supporting Information for

## Enhanced Ionic Accessibility of Flexible MXene Electrodes Produced by Natural Sedimentation

Ning Sun<sup>1, †</sup>, Zhaoruxin Guan<sup>1, †</sup>, Qizhen Zhu<sup>1</sup>, Babak Anasori<sup>2, 3</sup>, Yury Gogotsi<sup>2, \*</sup>, Bin Xu<sup>1, \*</sup>

<sup>1</sup>State Key Laboratory of Organic-Inorganic Composites, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

<sup>2</sup>Department of Materials Science and Engineering and A. J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA 19104, USA

<sup>3</sup>Integrated Nanosystems Development Institute, Department of Mechanical and Energy Engineering, Purdue School of Engineering and Technology, Indiana University – Purdue University Indianapolis, Indianapolis, IN 46202, USA

<sup>†</sup>Ning Sun and Zhaoruxin Guan contributed equally to this work

\*Corresponding authors. E-mail: binxumail@163.com or xubin@mail.buct.edu.cn (B. Xu), gogotsi@drexel.edu (Y. Gogotsi)

### Supplementary Tables and Figures

**Table S1**  $2\theta$  for the split (002) peaks and the calculated interlayer distances of the conventional vacuum-filtered MXene film and natural-sedimented MXene films

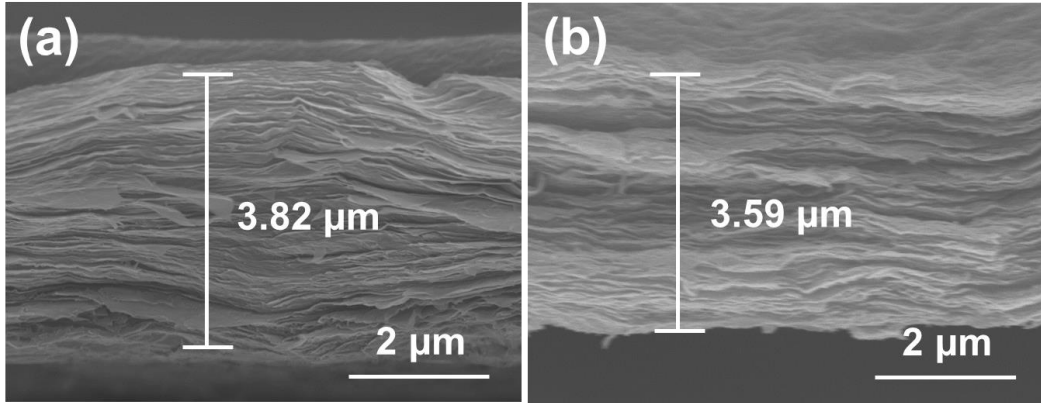
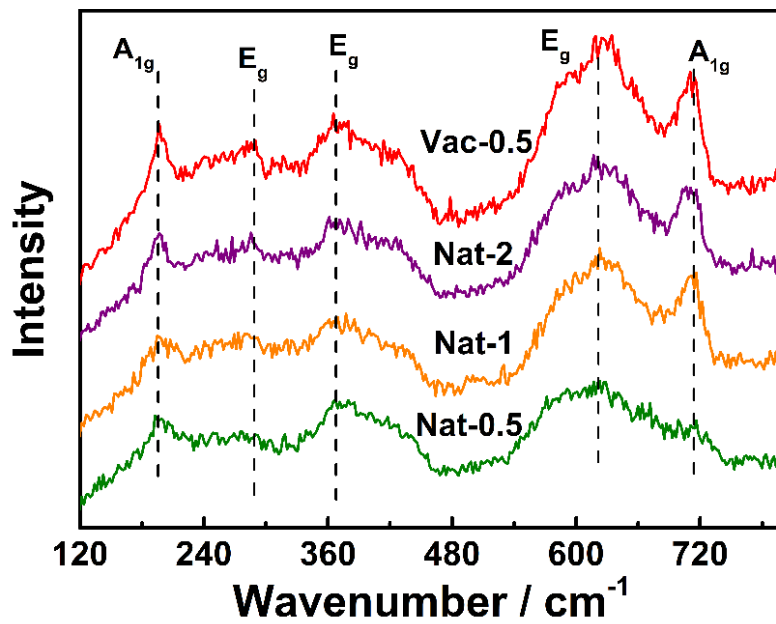
	high-angle peak		low-angle peak	
	$2\theta$	$d$ (Å)	$2\theta$	$d$ (Å)
<b>Vac-0.5</b>	7.24	12.20	6.28	14.06
<b>Nat-2</b>	7.17	12.32	6.08	14.52
<b>Nat-1</b>	7.10	12.44	6.03	14.64
<b>Nat-0.5</b>	7.03	12.56	5.98	14.76

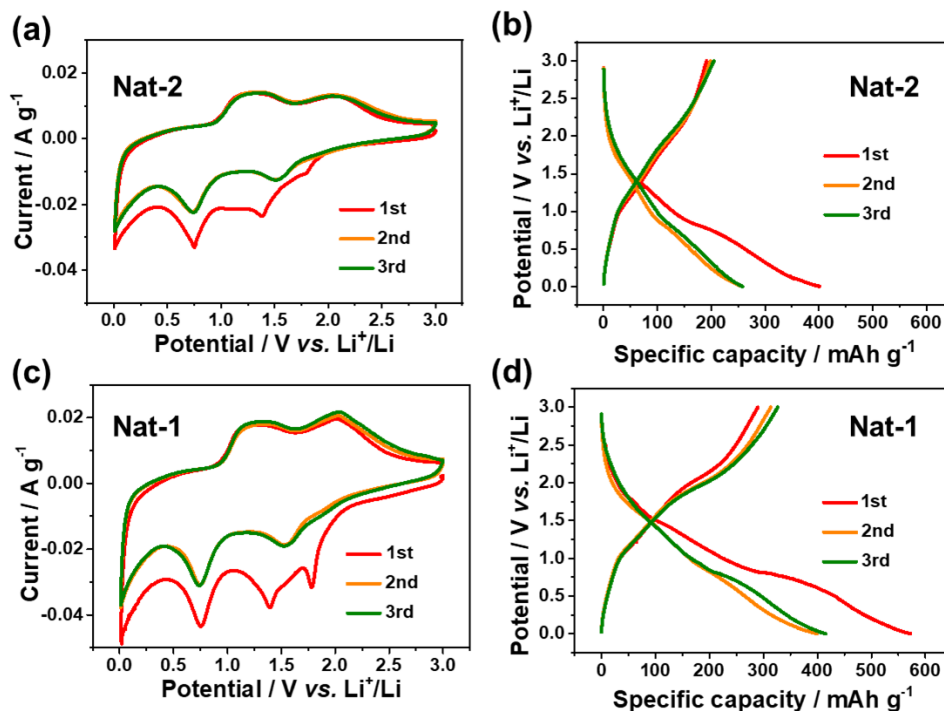
**Table S2** Comparison of lithium storage performance between naturally-sedimented MXene and other reported pure  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene anode materials

Electrode material	Li-storage capacity	Cycle performance	Rate performance	Refs.
<b>Free-standing <math>\text{Ti}_3\text{C}_2\text{T}_x</math> MXene film prepared by natural sedimentation</b>	<b>351 mAh g<sup>-1</sup> at 30 mA g<sup>-1</sup></b>	<b>242 mAh g<sup>-1</sup> at 320 mA g<sup>-1</sup> over 1000 cycles (no capacity loss)</b>	<b>115 mAh g<sup>-1</sup> at 500 mA g<sup>-1</sup></b>	<b>This work</b>
Heteroatom-controlled $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films by annealing	221 mAh g <sup>-1</sup> at 32 mA g <sup>-1</sup>	~100 mAh g <sup>-1</sup> at 320 mA g <sup>-1</sup> over 500 cycles	124 mAh g <sup>-1</sup> at 320 mA g <sup>-1</sup>	[S1]
Free-standing $\text{Ti}_3\text{C}_2\text{T}_x$ electrode prepared by cold pressed	120 mAh g <sup>-1</sup> at 30 mA g <sup>-1</sup> (electrode thickness: 220 $\mu\text{m}$ )	28 mAh g <sup>-1</sup> over 50 cycles		[S2]
$\text{Al}^{3+}$ pre-intercalated $\text{Ti}_3\text{C}_2\text{T}_x$ film electrode	157.6 mAh g <sup>-1</sup> at 1 C	Retaining 85% over 100 cycles	42.5 mAh g <sup>-1</sup> at 5 C	[S3]
Low-F $\text{Ti}_3\text{C}_2$ MXene film prepared by annealing	~123.7 mAh cm <sup>-3</sup> at 1 C	Retaining 75% over 100 cycles	~50 mAh cm <sup>-3</sup> at 5 C	[S4]
$\text{Ti}_3\text{C}_2\text{T}_x$ MXene film treated with hydrazine vapor and annealing	~180 mAh g <sup>-1</sup> at 100 mA g <sup>-1</sup>	56.4 mAh g <sup>-1</sup> at 1A g <sup>-1</sup> over 1000 cycles	80 mAh g <sup>-1</sup> at 1 A g <sup>-1</sup>	[S5]
$\text{Ti}_3\text{C}_2\text{T}_x$ paper prepared by intercalation with hydrazine monohydrate	410 mAh g <sup>-1</sup> at 1 C	—	—	[S6]
Porous $\text{Ti}_3\text{C}_2\text{T}_x$ film	~110 mAh g <sup>-1</sup> at 0.5 C	Retaining ~100% over 100 cycles		[S7]
$\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT}$ composite films (9:1)	220 mAh g <sup>-1</sup> at 0.5 C	Retaining ~100% over 100 cycles		[S7]
Porous $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT}$ composite films (9:1)	650 mAh g <sup>-1</sup> at 0.1 C	Capacity increases over 100 cycles	~230 mAh g <sup>-1</sup> at 10 C	[S7]
$\text{Ti}_3\text{C}_2/\text{CNTs}$ hybrid film (1:1)	403.5 mAh g <sup>-1</sup> at 0.5 C	428.1 mAh g <sup>-1</sup> over 300 cycles	218.2 mAh g <sup>-1</sup> at 2 C	[S8]
$\text{Ti}_3\text{C}_2$ intercalated with DMSO	~210 mAh g <sup>-1</sup> at 26 mA g <sup>-1</sup>	118 mAh g <sup>-1</sup> at 260 mA g <sup>-1</sup> over 75 cycles	123.6 mAh g <sup>-1</sup> at 260 mA g <sup>-1</sup>	[S9]
Nitrogen containing $\text{Ti}_3\text{C}_2$ prepared by heat treatment in $\text{NH}_3$	~250 mAh g <sup>-1</sup> at 32 mA g <sup>-1</sup>		168 mAh g <sup>-1</sup> at 320 mA g <sup>-1</sup>	[S10]
Multilayer $\text{Ti}_3\text{C}_2$ MXene improved by calcination	254.6 mAh g <sup>-1</sup> at 0.1 C	147.4 mAh g <sup>-1</sup> at 1 C over 100 cycles	120 mAh g <sup>-1</sup> at 4 C	[S11]

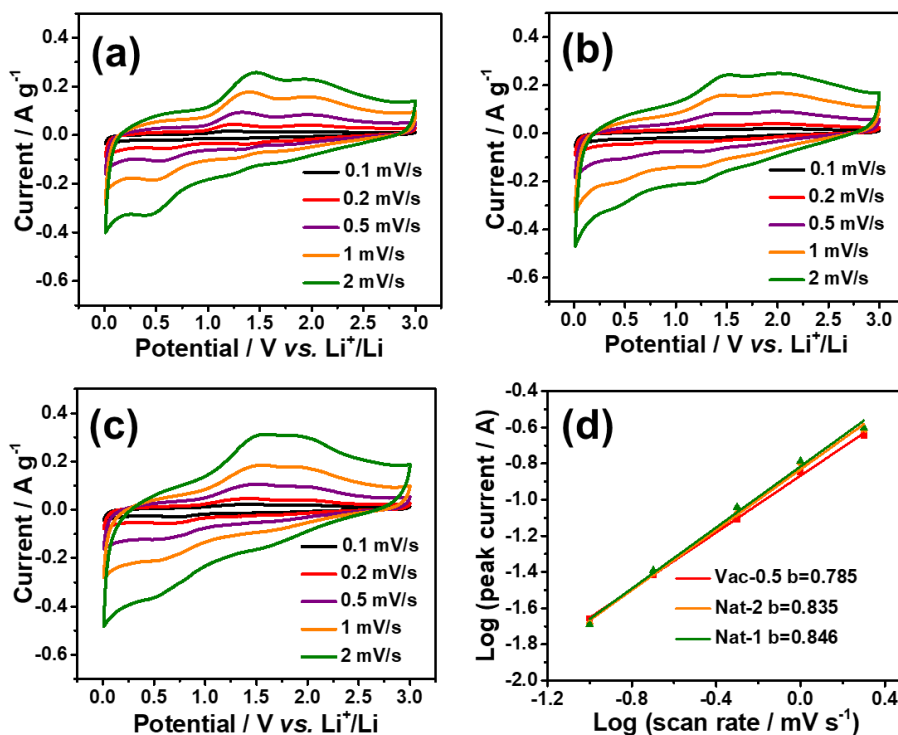
**Table S3** The fitting resistance of the obtained MXene films

	Vac-0.5	Nat-2	Nat-1	Nat-0.5
$R_e$ ( $\Omega$ )	8.9	5.1	4.3	3.1
$R_{ct}$ ( $\Omega$ )	105.2	89.2	67.5	49.7
$R_{Li}$ ( $\Omega$ )	595.6	540.9	347.1	325.6

**Fig. S1** Cross-sectional SEM images of Nat-1 film (a) and Nat-2 film (b)**Fig. S2** Raman spectra of the as-prepared MXene films



**Fig. S3** CV profiles at  $0.1 \text{ mV s}^{-1}$  and galvanostatic charge/discharge curves at  $30 \text{ mA g}^{-1}$  for the initial three cycles of Nat-2 film (a, b) and Nat-1 film (c, d)



**Fig. S4** CV curves at various scan rates ranging from  $0.1$  to  $2 \text{ mV s}^{-1}$  of Vac-0.5 (a), Nat-2 (b) and Nat-1 (c) and the relationships between the peak current and scan rate for the anodic peak at  $\sim 2.0 \text{ V}$  of the prepared MXene films (d)

## Supplementary References

- [S1] Zhang H., Xin X., Liu H., Huang H., Chen N., et al., Enhancing lithium adsorption and diffusion toward extraordinary lithium storage capability of freestanding  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene. *J. Phys. Chem. C* **123**(5), 2792-2800 (2019). <https://doi.org/10.1021/acs.jpcc.8b11255>
- [S2] Kim S.J., Naguib M., Zhao M.Q., Zhang C.F., Jung H.T., Barsoum M.W., Gogotsi Y., High mass loading, binder-free MXene anodes for high areal capacity Li-ion batteries. *Electrochim. Acta* **163**, 246-251 (2015). <https://doi.org/10.1016/j.electacta.2015.02.132>
- [S3] Lu M., Han W., Li H., Shi W., Wang J., et al., Tent-pitching-inspired high-valence period 3-cation pre-intercalation excels for anode of 2D titanium carbide (MXene) with high Li storage capacity. *Energy Storage Mater.* **16**, 163-168 (2019). <https://doi.org/10.1016/j.ensm.2018.04.029>
- [S4] Lu M., Li H., Han W., Chen J., Shi W., et al., 2D titanium carbide (MXene) electrodes with lower-F surface for high performance lithium-ion batteries. *J. Energy. Chem.* **31**, 148-153 (2019). <https://doi.org/10.1016/j.jechem.2018.05.017>
- [S5] Ma Z., Zhou X., Deng W., Lei D., Liu Z., 3D porous MXene ( $\text{Ti}_3\text{C}_2$ )/reduced graphene oxide hybrid films for advanced lithium storage. *ACS Appl. Mater. Interfaces* **10**(4), 3634-3643 (2018). <https://doi.org/10.1021/acsami.7b17386>
- [S6] Mashtalir O., Naguib M., Mochalin V.N., Dall'Agnese Y., Heon M., Barsoum M. W., Gogotsi Y., Intercalation and delamination of layered carbides and carbonitrides. *Nat. Commun.* **4**, 1716 (2013). <https://doi.org/10.1038/ncomms2664>
- [S7] Ren C.E., Zhao M.Q., Makaryan T., Halim J., Boota M., et al., Porous two-dimensional transition metal carbide (MXene) flakes for high-performance Li-ion storage. *Chemelectrochem* **3**(5), 689-693 (2016). <https://doi.org/10.1002/celec.201600059>
- [S8] Liu Y., Wang W., Ying Y., Wang Y., Peng X., Binder-free layered  $\text{Ti}_3\text{C}_2$ /CNTs nanocomposite anodes with enhanced capacity and long-cycle life for lithium-ion batteries. *Dalton Trans.* **44**(16), 7123-7126 (2015). <https://doi.org/10.1039/c4dt02058h>
- [S9] Sun D., Wang M., Li Z., Fan G., Fan L.-Z., Zhou A., Two-dimensional  $\text{Ti}_3\text{C}_2$  as anode material for Li-ion batteries. *Electrochem. Commun.* **47**, 80-83 (2014). <https://doi.org/10.1016/j.elecom.2014.07.026>

- [S10] Cheng R., Hu T., Zhang H., Wang C., Hu M., et al., Understanding the lithium storage mechanism of  $\text{Ti}_3\text{C}_2\text{T}_x$  mxene. *J. Phys. Chem. C* **123**(2), 1099-1109 (2018). <https://doi.org/10.1021/acs.jpcc.8b10790>
- [S11] Kong F., He X., Liu Q., Qi X., Zheng Y., Wang R., Bai Y., Improving the electrochemical properties of MXene  $\text{Ti}_3\text{C}_2$  multilayer for Li-ion batteries by vacuum calcination. *Electrochim. Acta* **265**, 140-150 (2018). <https://doi.org/10.1016/j.electacta.2018.01.196>