Supplementary information

Recyclable HF-free $Ti_3C_2T_x$ 3D-printed supercapacitors: second life in sodium-ion batteries

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Table S1. The (0 0 2) position and d-spacing of $Ti_3C_2T_x$ Mxene synthesised using different techniques.

Method	Etchant	Temperature	Duration	(0 0 2) peak position	d-spacing (Å)	c-LP (Å)	Reference
Molten Salt	$CuCl_2$:KCl:NaCl	680 °C	24 hours	8.07°	10.94		[1]
Molten Salt (Insitu preparation of MAX and etching)	$CuCl_2$:KCl:NaCl	700 °C	10 hour : 10 min		11.07	22.13	[2]
Molten Salt	SnF_2	550 °C	6 hours	9.4°			[3]
Molten Salt	$CuCl_2$:KCl:NaCl	700 °C	40 min	7.94°	11.1		[4]
Acid etching	20% HF	Room temperature	11 hours	8.9 °			[5]
Insitu HF etching method	6M HCl:LiF	40 °C	40 hours	6.9°			[6]
HF etching	Conc. HF	Room temperature	10 hours	-	-	-	[7]
Wet-etching alkalization strategy	Fluoride salts	Room Temperature			12 to 15		[8]
Acid solution etching	HF	Room temperature	24 hours	9°	19.62		[9]
Acid solution etching	LiF:HCl	60 °C	50 hours	7.67°	22.05		[9]
Acid solution etching	FeF_3:HCl	60 °C	25 hours	8.01°	23.02		[9]
Molten Salt	KF:NaF:oxalic acid dihydrate	400 °C	10 hours	6.9		25.72	This work

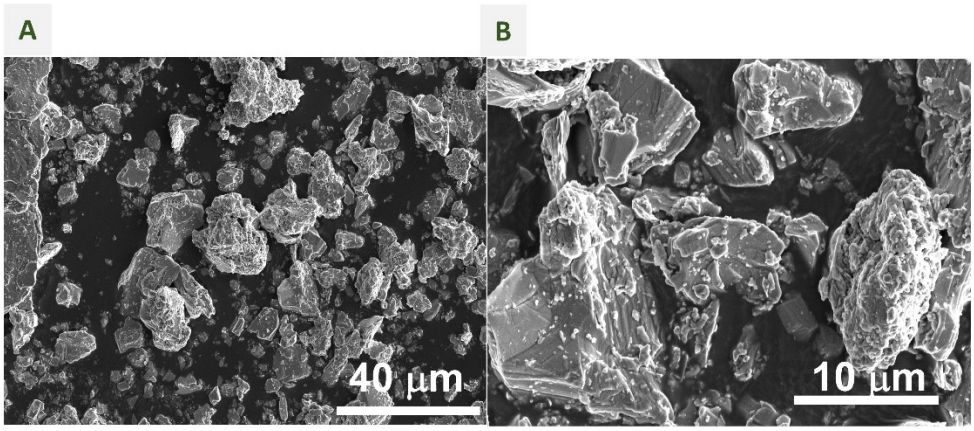

Figure S1. SEM images of MSTC-00 at different magnifications.

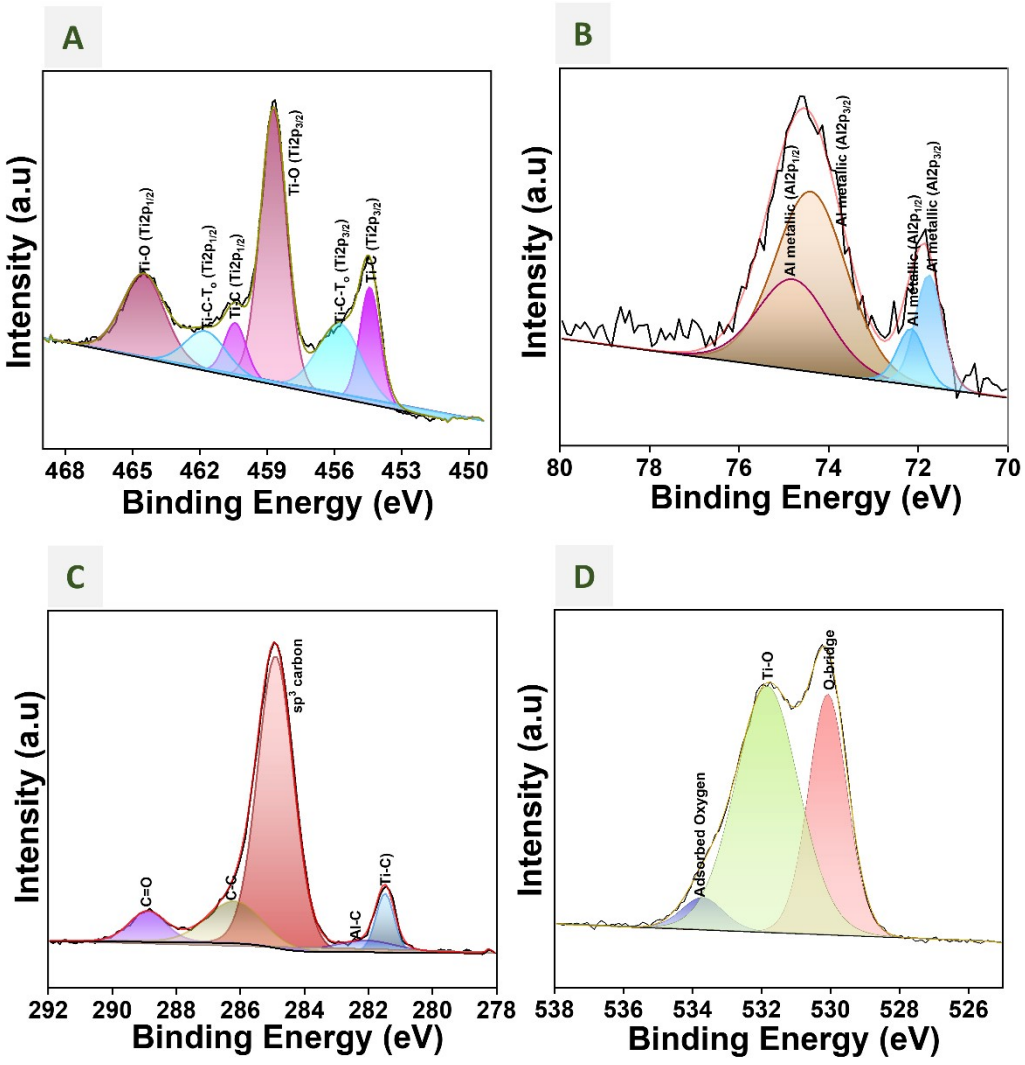

Figure S2. High resolution XPS of (A) Ti 2p, (B) Al 2p, (C) C 1s and (D) O 1s of Ti_3AlC_2 MAX phase.

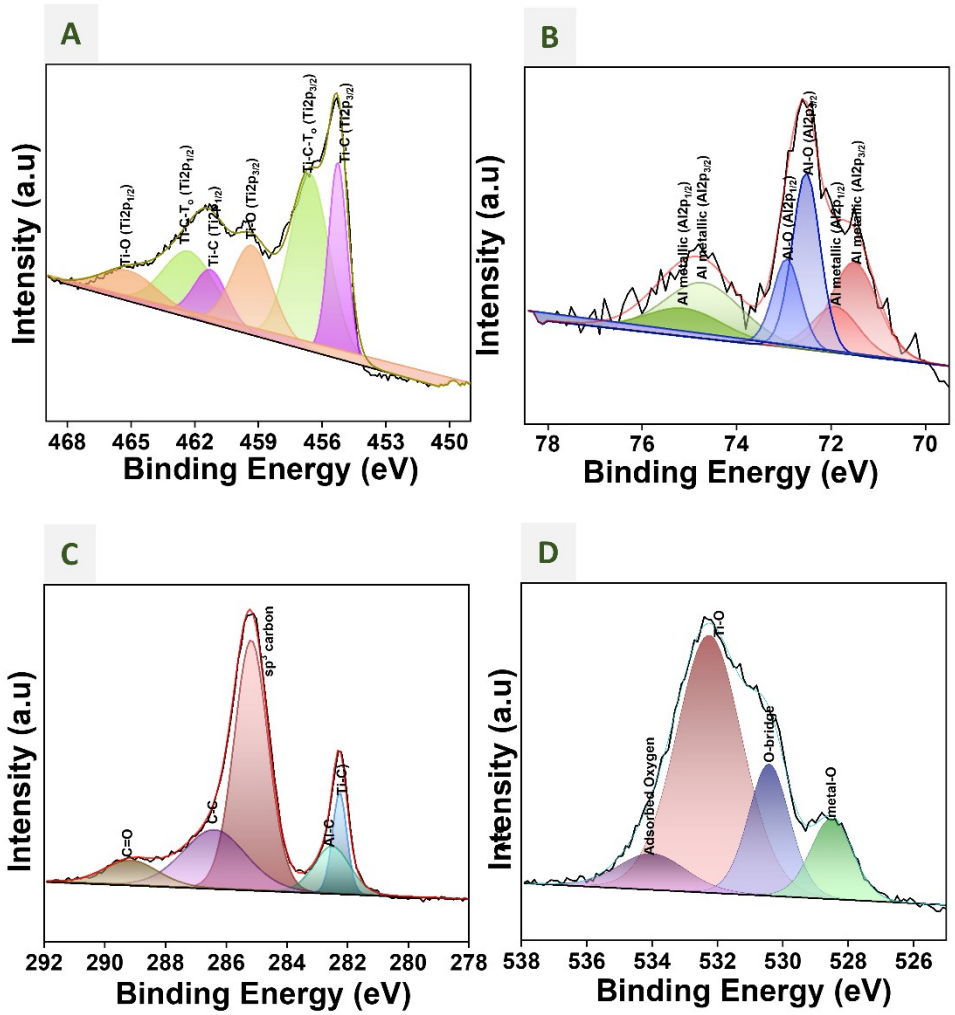

Figure S3. High resolution XPS of (A) Ti 2p, (B) Al 2p, (C) C 1s and (D) O 1s of MSTC-00.

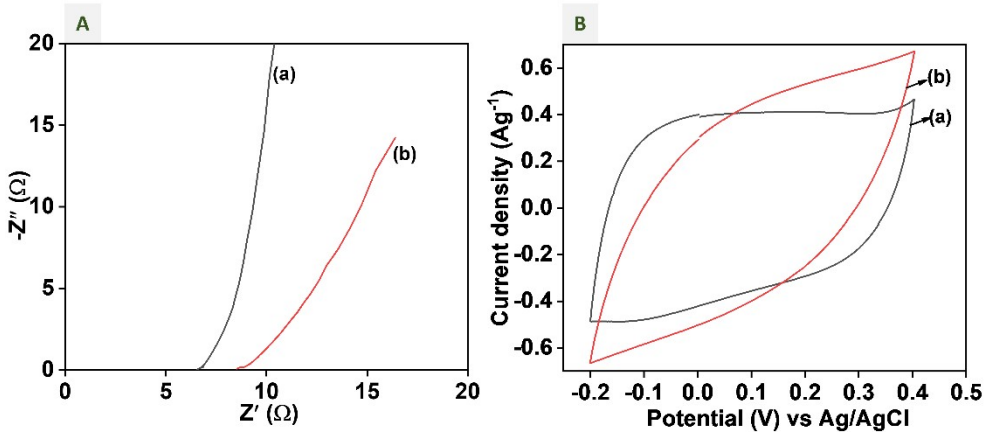

Figure S4. (A) Nyquist plots and (B) cyclic voltammograms of (a) commercial Ti_3C_2 and (b) MSTC-OX.

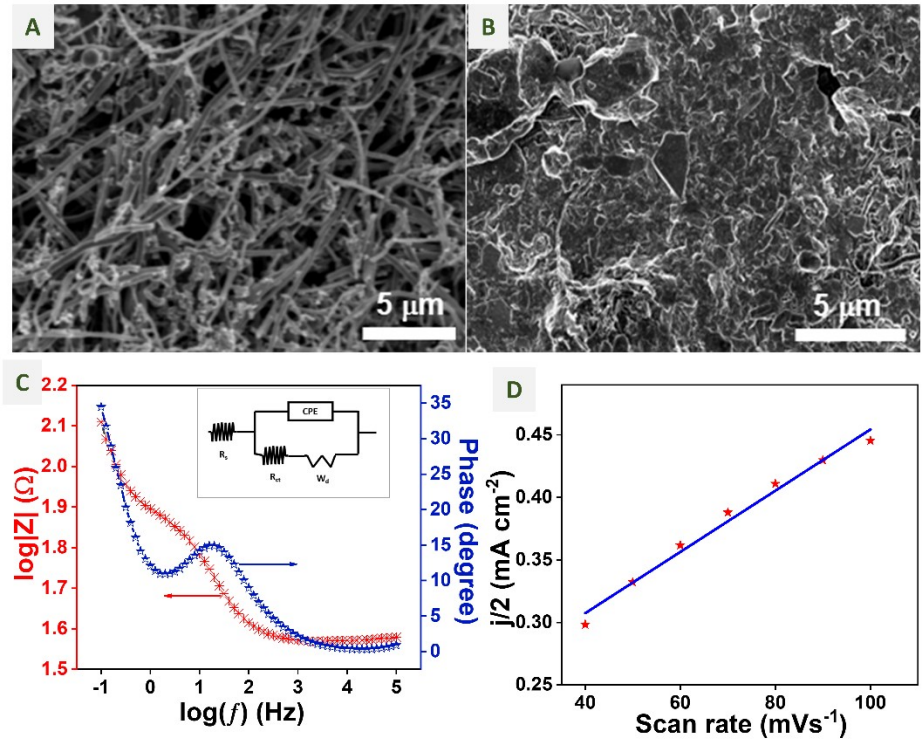

Figure S5. SEM images of (A) activated 3DE and (B) TC-3DE. (C) Bode plots of TC-3DE (inset: equivalent circuit), and (D) current density versus scan rate curves of TC-3DE in 1 M H_2SO_4 against Ag/AgCl (3M KCl).

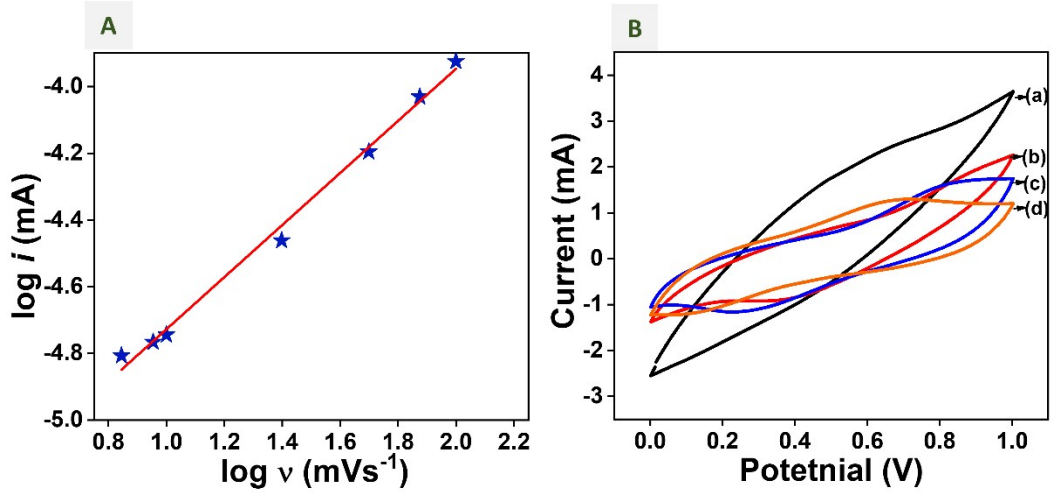

Figure S6. (A) log *i* versus log ν curves of TC-3DE supercapacitors and (B) cyclic voltammograms of symmetric TC-3DE cell for 5000 cycles (cycle (a) 2nd, (b) 500th, (c) 1000th, (d) 5000th.

Table S2. Performance of 3D printed $Ti_3C_2T_x$ based supercapacitors.

Material	Electrolyte (Gel)	Specific capacity	Energy Density	Power density	Reference
2D $Ti_3C_2T_x$ microsupercapcitor MSC-1	PVA/H_2SO_4	1 F cm^{-2} at 2mV S^{-1}	56 mW h cm^{-3}	24.9 W cm^{-3},	[10]
3D Printed $Ti_3C_2T_x$ MXene/Cellulose Nanofiber	PVA/H_2SO_4	70 Fg^{-1} at 1 mA cm^{-2}	101 μWh cm^{-2}	0.299 mW cm^{-2}	[11]
$Ti_3C_2T_x$ coated carbon nanofiber structural supercapcitors	Li-G3]TFSI	908 mF/g^{-1} at 0.5 mA g^{-1}			[12]
WCF-ZnCoSe-Mxene		14.55 F g^{-1}	2.02 Wh kg^{-1}	36.75 Wkg^{-1}	[13]
WCF-N@ZnCoSe-mxene		19.36 F g^{-1}	2.69 Wh kg^{-1}	43.20 Wkg^{-1}	[13]
MXene@PTC-12 h	PVA/H_2SO_4				[14]
TC-3DE supercapacitors	Xanthan gum/H_2SO_4	30 Fg^{-1}	1.767 $Whkg^{-1}$	20.64 Wkg^{-1}	This work

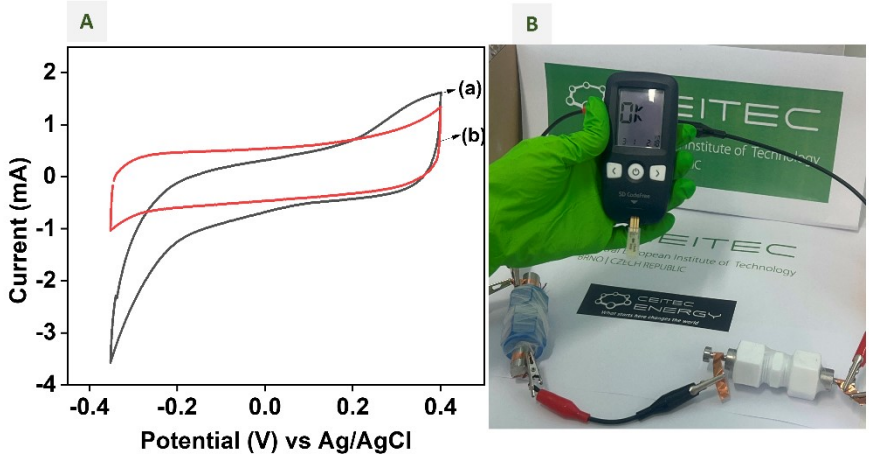

Figure S7. Cyclic voltammograms of sodium composite in (a) 1M H_2SO_4 and (b) recycled 1M sodium lactate. (B) photograph of a glucometer powered up using SIB-a cells.

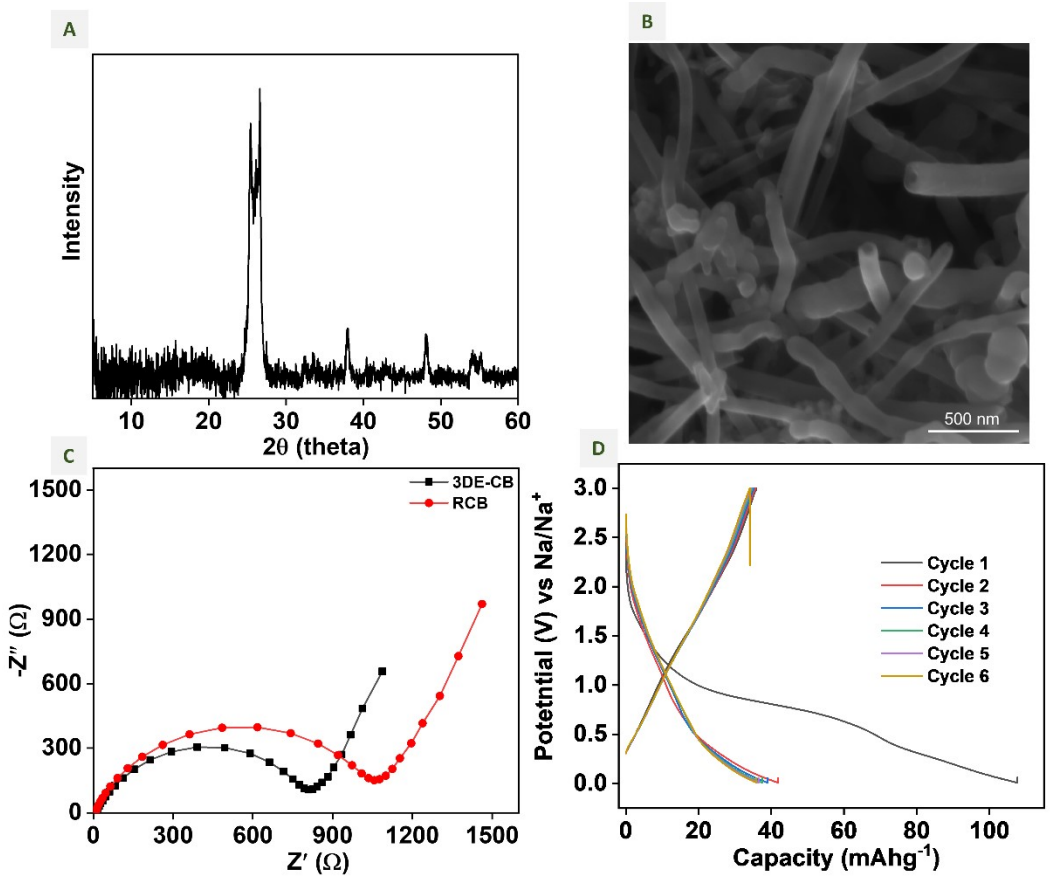

Figure S8. (A) XRD pattern, (B) SEM image of 3DE-CB (carbon black extracted from fresh PLA/Graphene filament). (C) Nyquist plot and (D) GCD curves (at 0.3C rate) of SIB-c cells.

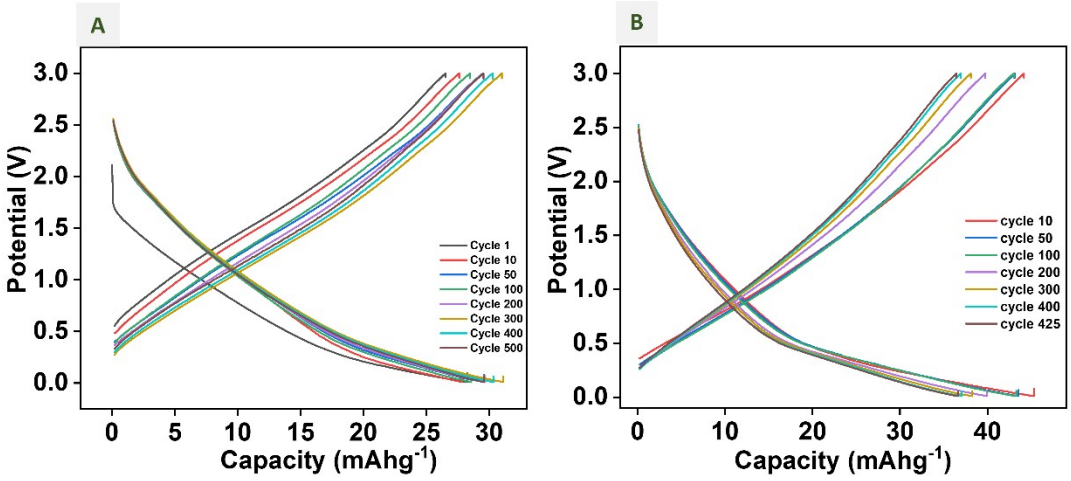

Figure S9. GCD curve of (A) SIB-a and (B) SIB-b cells for 500 cycles at 1C-rate.

References

(1) Liu, L.; Orbay, M.; Luo, S.; Duluard, S.; Shao, H.; Harmel, J.; Rozier, P.; Taberna, P.-L.; Simon, P. Exfoliation and Delamination of Ti3C2Tx MXene Prepared via Molten Salt Etching Route. *ACS Nano* **2022**, *16* (1), 111-118. DOI: 10.1021/acsnano.1c08498.

(2) Ma, G.; Shao, H.; Xu, J.; Liu, Y.; Huang, Q.; Taberna, P.-L.; Simon, P.; Lin, Z. Li-ion storage properties of two-dimensional titanium-carbide synthesized via fast one-pot method in air atmosphere. *Nature Communications* **2021**, *12* (1), 5085. DOI: 10.1038/s41467-021-25306-y.

(3) Arole, K.; Blivin, J. W.; Saha, S.; Holta, D. E.; Zhao, X.; Sarmah, A.; Cao, H.; Radovic, M.; Lutkenhaus, J. L.; Green, M. J. Water-dispersible Ti3C2Tz MXene nanosheets by molten salt etching. *iScience* **2021**, *24* (12), 103403. DOI: https://doi.org/10.1016/j.isci.2021.103403.

(4) Chen, J.; Jin, Q.; Li, Y.; Shao, H.; Liu, P.; Liu, Y.; Taberna, P.-L.; Huang, Q.; Lin, Z.; Simon, P. Molten Salt-Shielded Synthesis (MS3) of MXenes in Air. *ENERGY & ENVIRONMENTAL MATERIALS* **2023**, *6* (2), e12328. DOI: https://doi.org/10.1002/eem2.12328.

(5) Wang, G.; Yang, Z.; Wu, L.; Wang, J.; Liu, X. Studies on improved stability and electrochemical activity of titanium carbide MXene-polymer nanocomposites. *Journal of Electroanalytical Chemistry* **2021**, *900*, 115708. DOI: https://doi.org/10.1016/j.jelechem.2021.115708.

(6) Saha, S.; Arole, K.; Radovic, M.; Lutkenhaus, J. L.; Green, M. J. One-step hydrothermal synthesis of porous Ti3C2Tz MXene/rGO gels for supercapacitor applications. *Nanoscale* **2021**, *13* (39), 16543-16553, 10.1039/D1NR02114A. DOI: 10.1039/D1NR02114A.

(7) Syamsai, R.; Kollu, P.; Kwan Jeong, S.; Nirmala Grace, A. Synthesis and properties of 2D-titanium carbide MXene sheets towards electrochemical energy storage applications. *Ceramics International* **2017**, *43* (16), 13119-13126. DOI: https://doi.org/10.1016/j.ceramint.2017.07.003.

(8) Xu, Z.; Zhang, Y.; Liu, M.; Meng, Q.; Shen, C.; Xu, L.; Zhang, G.; Gao, C. Two-dimensional titanium carbide MXene produced by ternary cations intercalation via structural control with angstrom-level precision. *iScience* **2022**, *25* (12), 105562. DOI: https://doi.org/10.1016/j.isci.2022.105562.

(9) Wang, X.; Garnero, C.; Rochard, G.; Magne, D.; Morisset, S.; Hurand, S.; Chartier, P.; Rousseau, J.; Cabioc'h, T.; Coutanceau, C.; et al. A new etching environment (FeF3/HCl) for the synthesis of two-dimensional titanium carbide MXenes: a route towards selective reactivity vs. water. *Journal of Materials Chemistry A* **2017**, *5* (41), 22012-22023, 10.1039/C7TA01082F. DOI: 10.1039/C7TA01082F.

(10) Orangi, J.; Hamade, F.; Davis, V. A.; Beidaghi, M. 3D Printing of Additive-Free 2D Ti3C2Tx (MXene) Ink for Fabrication of Micro-Supercapacitors with Ultra-High Energy Densities. *ACS Nano* **2020**, *14* (1), 640-650. DOI: 10.1021/acsnano.9b07325.

(11) Zhou, G.; Li, M.-C.; Liu, C.; Wu, Q.; Mei, C. 3D Printed Ti3C2Tx MXene/Cellulose Nanofiber Architectures for Solid-State Supercapacitors: Ink Rheology, 3D Printability, and Electrochemical Performance. *Advanced Functional Materials* **2022**, *32* (14), 2109593. DOI: https://doi.org/10.1002/adfm.202109593.

(12) Dharmasiri, B.; Usman, K. A. S.; Qin, S. A.; Razal, J. M.; Tran, N. T.; Coia, P.; Harte, T.; Henderson, L. C. Ti3C2Tx MXene coated carbon fibre electrodes for high performance structural supercapacitors. *Chemical Engineering Journal* **2023**, *476*, 146739. DOI: https://doi.org/10.1016/j.cej.2023.146739.

(13) Deka, B. K.; Hazarika, A.; Kang, G.-H.; Hwang, Y. J.; Jaiswal, A. P.; Chan Kim, D.; Park, Y.-B.; Park, H. W. 3D-Printed Structural Supercapacitor with MXene-N@Zn-Co Selenide Nanowire Based Woven Carbon Fiber Electrodes. *ACS Energy Letters* **2023**, *8* (2), 963-971. DOI: 10.1021/acsenergylett.2c02505.

(14) Zhu, G.; Hou, Y.; Lu, J.; Zhang, H.; Zhuang, Z.; Baig, M. M.; Khan, M. Z.; Akram, M. A.; Dong, S.; Liu, P.; et al. MXene decorated 3D-printed carbon black-based electrodes for solid-state micro-supercapacitors. *Journal of Materials Chemistry A* **2023**, *11* (46), 25422-25428, 10.1039/D3TA04573K. DOI: 10.1039/D3TA04573K.