Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Investigating the Local Structure of Ti Based MXene Materials by Temperature Dependent X-Ray Absorption Spectroscopy

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X-RAY DIFFRACTION MEASUREMENTS

X-ray diffraction (XRD) measurements were performed using a Rigaku RINT-TTR III powder diffractometer with Cu Kα radiation (λ = 1.5406 Å) in Bragg-Brentano geometry. A scattered intensity was recorded within a 2θ range of 5-80° with a step of 0.02°. Obtained XRD patterns are shown in Figure S1.

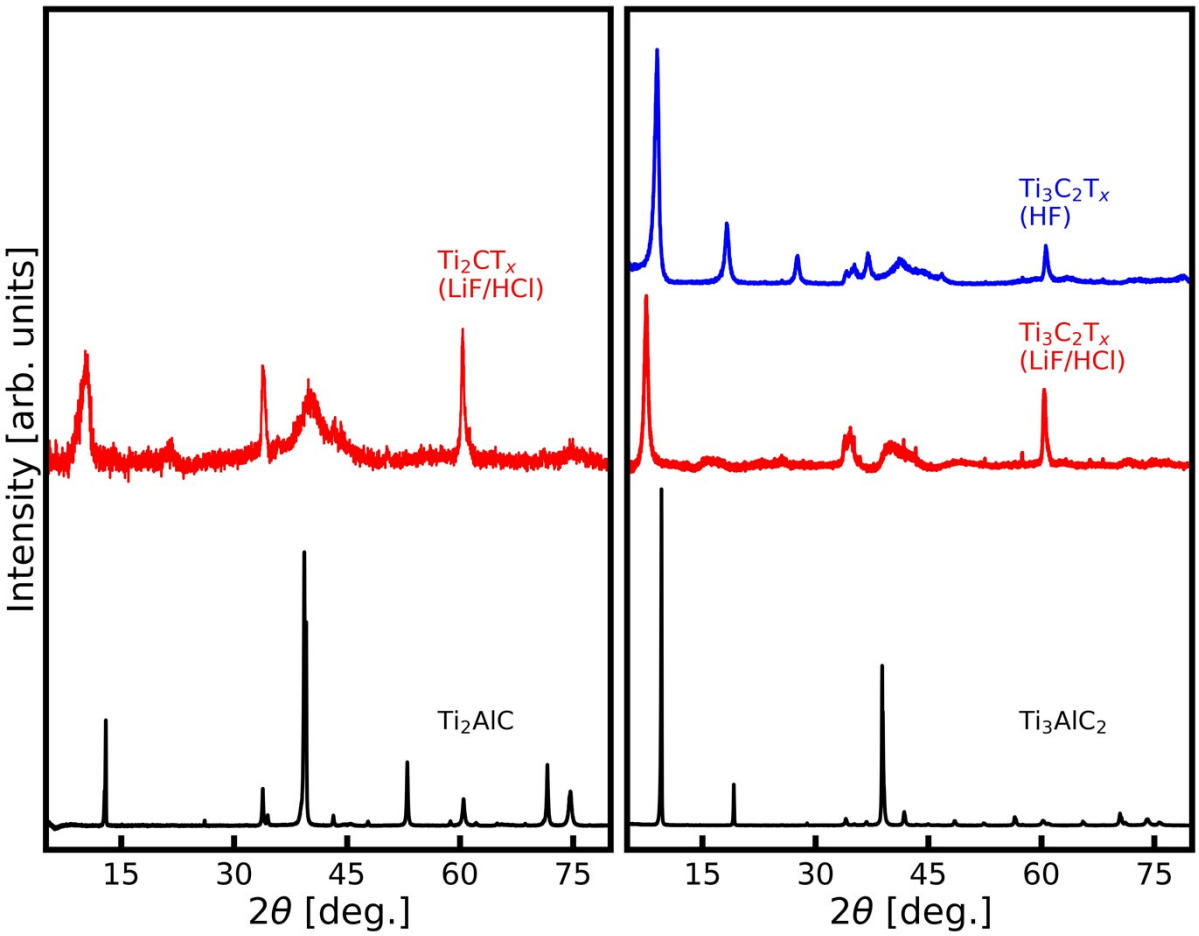

Figure S1: Powder X-ray diffraction patterns for a) Ti_2AlC, Ti_2CT_x (LiF/HCl etched); b) Ti_3AlC_2, $Ti_3C_2T_x$ (LiF/HCl etched), $Ti_3C_2T_x$ (HF etched) [S1-S3]

Obtained patterns confirm the successful synthesis of phase-pure samples and are similar to the ones reported in the literature for the same systems [S4-7].

EXAFS ANALYSIS

The Ti K-edge EXAFS signals analysis was based on the ab-initio real-space multiple scattering theory. Calculations of the scattering amplitude and phase shift functions were

performed, by the FEFF6 code, centred on a Ti atom and having a radius of 6 Å. The fits to experimental spectra were performed in the back-transformed *k* space by the means of FEFFIT code.

Initially, the fitting has been limited to the first two coordination shells around titanium atoms (Ti-C and Ti-Al or Ti-T_x), where the distances (R_i) and its corresponding Debye−Waller factor (σ_i^2), as well as, the coordination number (x) for Ti-T_x were the fitted parameters in the model. Successively, by fixing the obtained two first shells parameters, the next shells have been fitted, always keeping the number of free parameters below the maximum allowed number for an EXAFS fitting.

For all the scattering paths, except the Ti-T_x, the coordination numbers N_i were fixed to the average values known from diffraction studies [S8,S9]. E_0 and S_0^2 were empirically chosen by a number of fits on different scans done at lowest temperature. Then, during the temperature-dependent analysis, they were fixed to 1.3 eV and 0.55, respectively for all the samples.

REFERENCES

S1 S. Kajiyama, L. Szabova, H. Iinuma, A. Sugahara, K. Gotoh, K. Sodeyama, Y. Tateyama, M. Okubo and A. Yamada, Enhanced Li-Ion Accessibility in MXene Titanium Carbide by Steric Chloride Termination, *Adv. Energy Mater.*, 2017, **7**, 1–8.

S2 X. Wang, S. Kajiyama, H. Iinuma, E. Hosono, S. Oro, I. Moriguchi, M. Okubo and A. Yamada, Pseudocapacitance of MXene nanosheets for high-power sodium-ion hybrid capacitors, *Nat. Commun.*, 2015, **6**, 1–6.

S3 S. Kajiyama, L. Szabova, K. Sodeyama, H. Iinuma, R. Morita, K. Gotoh, Y. Tateyama, M. Okubo and A. Yamada, Sodium-Ion Intercalation Mechanism in MXene Nanosheets, *ACS Nano*, 2016, **10**, 3334–3341.

S4 Q. Luo, B. Chai, M. Xu, Q. Cai, Preparation and photocatalytic activity of TiO2-loaded Ti3C2 with small interlayer spacing, *Appl. Phys. A*, 2018, **124**, 495.

S5 N. Thakur, P. Kumar, D. C. Sati, R. Neffati and P. Sharma, Recent advances in two-dimensional MXenes for power and smart energy systems, *J. Energy Storage*, 2022, **50**, 104604.

S6 H. Aghamohammadi, R. Eslami-Farsani and E. Castillo-Martinez, Recent trends in the development of MXenes and MXene-based composites as anode materials for Li-ion batteries, *J. Energy Storage*, 2022, **47**, 103572.

S7 F. Liu, A. Zhou, J. Chen, H. Zhang, J. Cao, L. Wang, Q. Hu, Preparation and methane adsorption of two-dimensional carbide Ti2C, *Adsorption*, 2016, **22**, 915–922.

S8 M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi and M. W. Barsoum, Two-dimensional nanocrystals produced by exfoliation of Ti3AlC2, *Adv. Mater.*, 2011, **23**, 4248–4253.

S9 I. R. Shein and A. L. Ivanovskii, Graphene-like titanium carbides and nitrides Tin+1Cn, Tin+1Nn (n = 1, 2, and 3) from de-intercalated MAX phases: First-principles probing of their structural, electronic properties and relative stability, *Comput. Mater. Sci.*, 2012, **65**, 104–114.