

Supporting information

Temperature dependent swelling transitions in
Mxene $\text{Ti}_3\text{C}_2\text{T}_x$.

Artem Iakunkov,^a Andreas Nordenström,^a Nicolas Boulanger,^a Christoph Hennig,^{b,c} Igor Baburin,^d Alexandr Talyzin^{a}*

^aDepartment of Physics, Umeå University, Umeå, SE-901 87, Sweden.

^bInstitute of Resource Ecology, Helmholtz Zentrum Dresden Rossendorf, Bautzner Landstrasse 400, 01328, Dresden, Germany.

^cThe Rossendorf Beamline, European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38043 Grenoble, France.

^dTheoretische Chemie, Technische Universität Dresden, 01062, Dresden, Germany

1. Characterization of materials.

a) XPS data

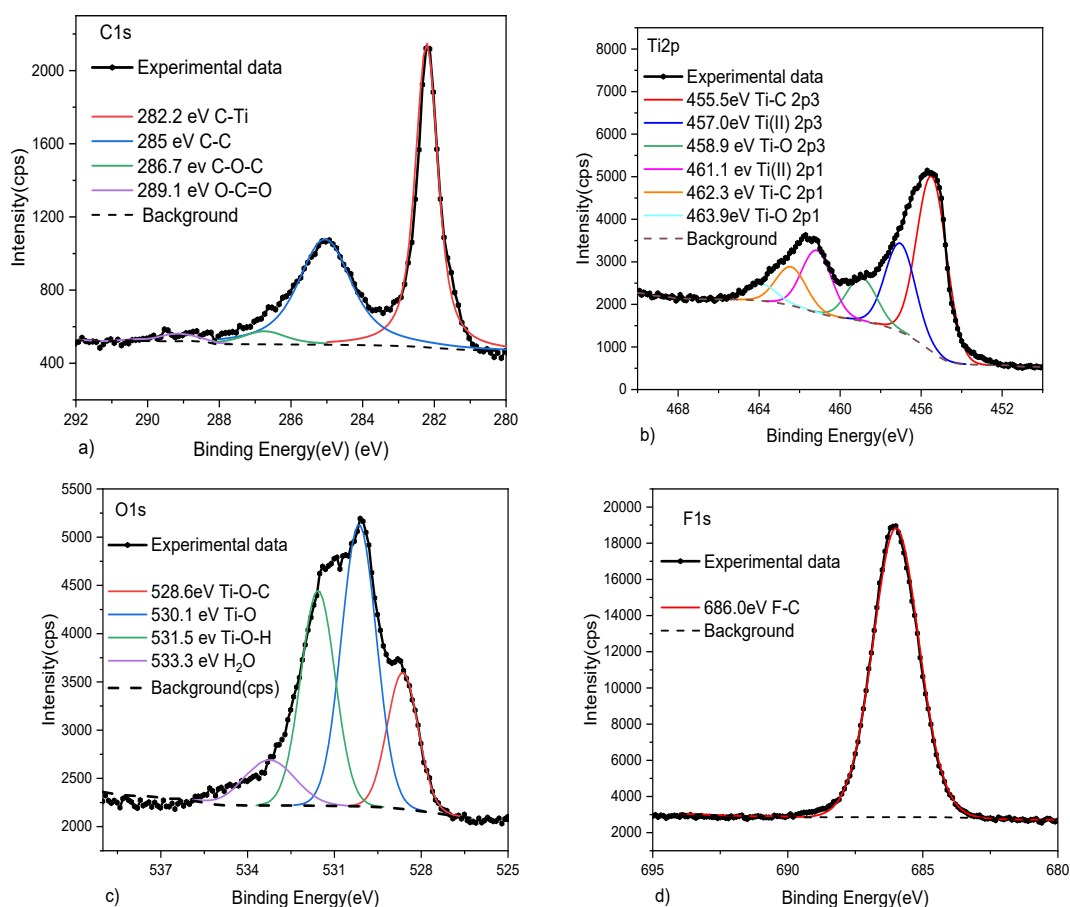


Figure S1. XPS for Mxene 2 prepared using LiCl+HF method: a) C1s ; b) Ti2p; c) O1s; d) F1s

Fitting and assignment of components are done according to ref.¹

XPS characterization of Mxene 1 and Mxene 2 (Figures S2 and S1) is in agreement with earlier reported data providing evidence for successful synthesis of materials. The complex chemical composition is reflected in XPS spectra which require several components for fitting of e.g. Ti2p and O1s components. It should be noted that detailed interpretation of XPS deconvolution results is somewhat different in existing literature and discussion of assignment is out of scope of this study. For example interpretation of 533.3 eV feature with absorbed water can be questioned since XPS is performed under UHV conditions and water is likely to escape at these conditions. Here we use most common variant of deconvolution^{1, 2} based on general expectations of Mxene composition.

The surface of 2D Mxene flakes is terminated by fluorine, oxygen and -OH groups with components related to the surface functionalization in Ti2p, O1s and C1s. The Mxene2 and Mxene 1 spectra are in general rather similar. The Mxene 1 shows somewhat stronger Ti-O component originating from TiO₂, while Mxene 2 shows some impurity of Al which is completely absent in Mxene 1 due to complete etching. The presence of Al impurity is also evident in O1s spectra.

As expected, both Mxenes show presence of Li intercalated into structure (10.9 at% and 7.4at% in Mxene 2 and Mxene 1 respectively). That is on the same level as reported in literature (6- at 10%) for Li intercalated Mxenes.

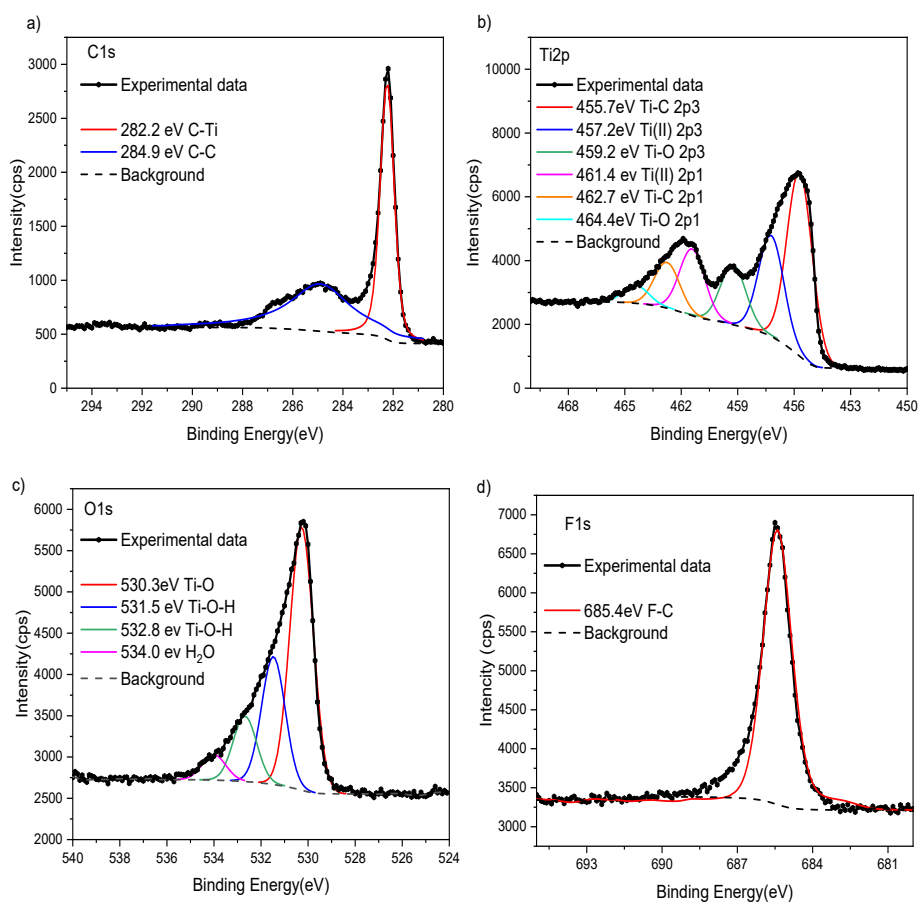


Figure S2. X-ray photoelectron spectra of Mxene 1 prepared using LiF+HCl a) C1s; b) Ti2p; c) O1s; d) F1s

As it is shown in the Figure 1 and 2 of main part, the swelling properties of Mxene 1 and Mxene 2 in water, acetonitrile and alcohols are rather similar. Both materials swell well in water and methanol, do not swell in acetonitrile and show almost no swelling in 1-alcohols longer than ethanol. Partial swelling of Mxene 2 in ethanol absent in Mxene 1 could be related to larger content of intercalated Li. The swelling of Li-intercalated Mxenes is believed to be related to hydration/solvation of Li cations. Alcohols are hydrophilic due to presence of -OH group but the alkyl chain is hydrophobic. Therefore, increase in the alcohol chain leads to overall less hydrophilic nature of molecules. The 2D layers of Mxene are rather heavy relative to e.g. graphene oxide and stronger hydration force (and swelling pressure) is required to move apart these layers. Therefore, absence of swelling in long alcohols is likely related to decrease in hydrophilicity of these molecules.

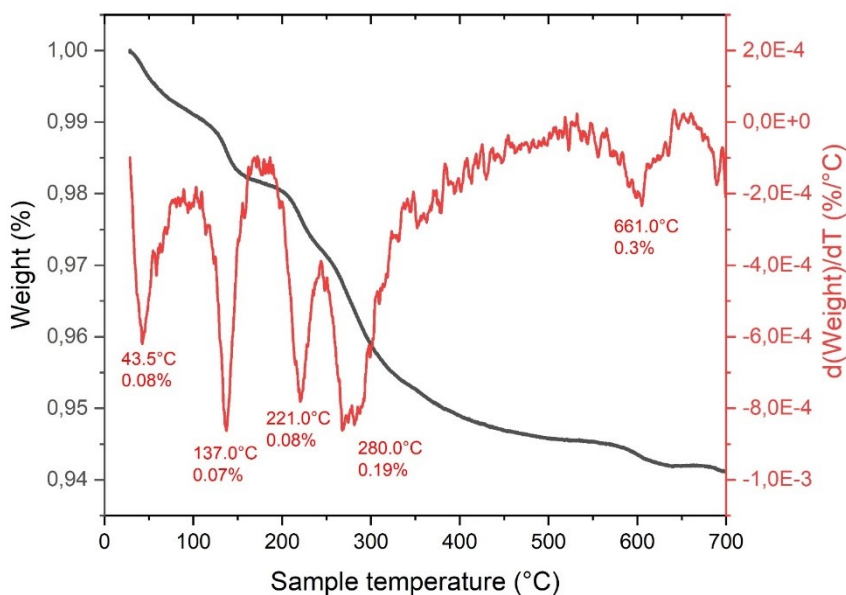
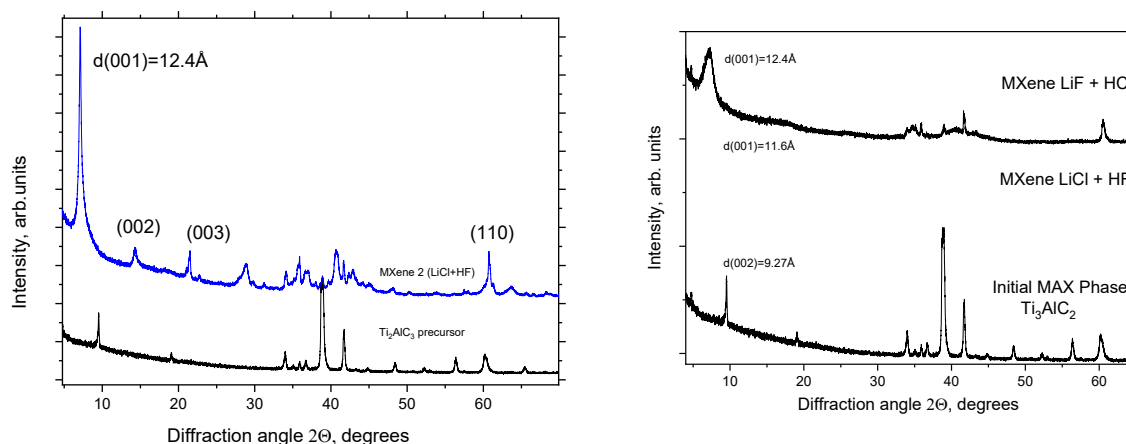


Figure S3. TGA curve (black) and 1st derivative of weight losses (red) recorded for MXene LiF+HCl using 5K per min heating rate under N₂ flow.

The TGA trace of MXene 1 shows several features expected from earlier studies. First step in weight loss curved occurs with maximum at 43.5°C and likely related to evaporation of physisorbed water. The water which solvates Cl in MXene interlayers escapes just above 100°C (onset) and differential peak at 137°C. The peaks found in the temperature region 200-280°C are likely to originate from detachment of oxygen containing functional groups from planar surface of MXene. According to mass spectrometry data some release of water is observed in this temperature range in agreement with deoxygenation process.³ Note that loss of hydroxyl and epoxy groups in graphene oxide is well known to occur in this temperature region but extends to higher temperatures up to 300-400°C due to functional groups located on the edges of flakes. Similar process is likely to occur also in MXene. It can be concluded that thermal degradation of MXene occurs above 200°C



a)

b)

Figure S4. XRD patterns of MXene 2 (a) synthesised using LiCl + HF etching and MXene 1 (b) synthesised using LiF + HCl compared to precursor Ti₃AlC₂ pattern. , CuK α radiation.

Figure S4 shows XRD patterns of MXene2 and Ti_2AlC_3 precursor. The figure proves complete conversion of precursor into MXene and absence of significant impurities (e.g. TiO_2) in a freshly prepared samples. .

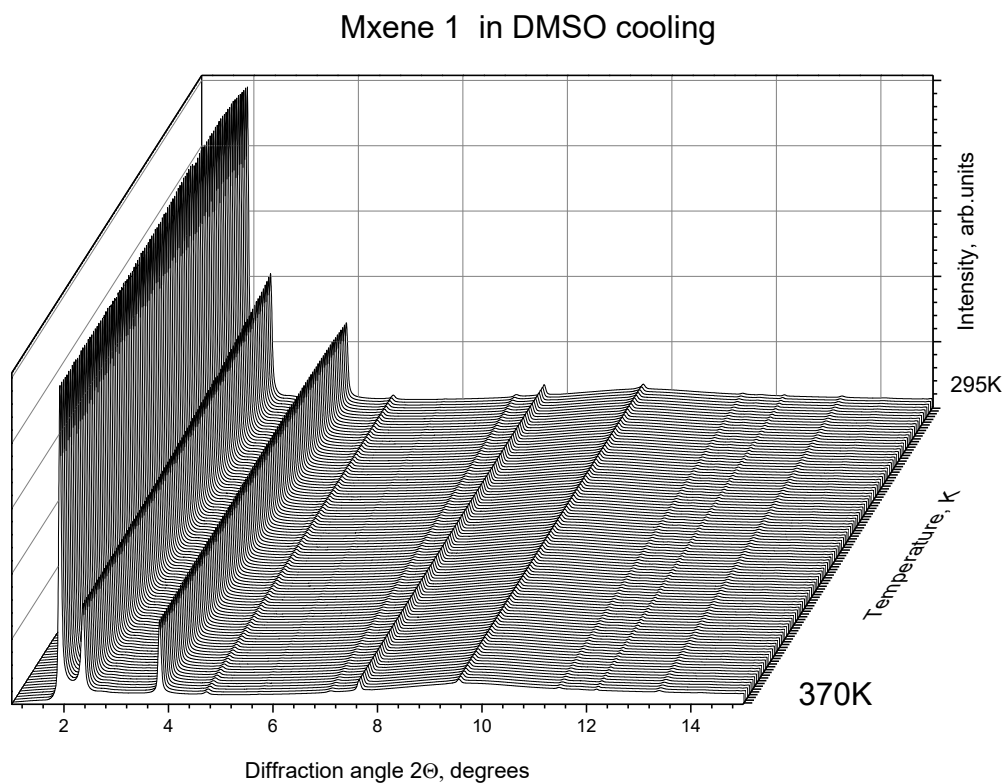
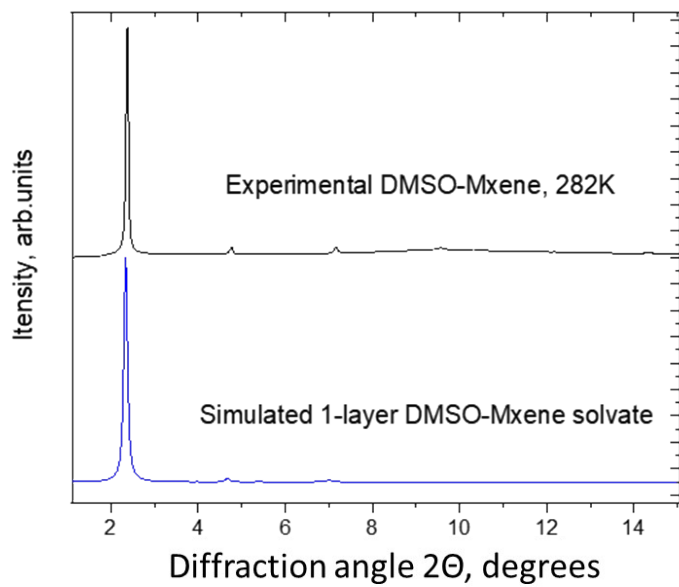


Figure S5 XRD patterns recorded from Mxene 1 immersed in DMSO upon cooling from 370K to ambient temperature (the patterns recorded in process of heating are shown in the main part). Radiation wavelength $\lambda=0.7381\text{\AA}$.

a)



b)

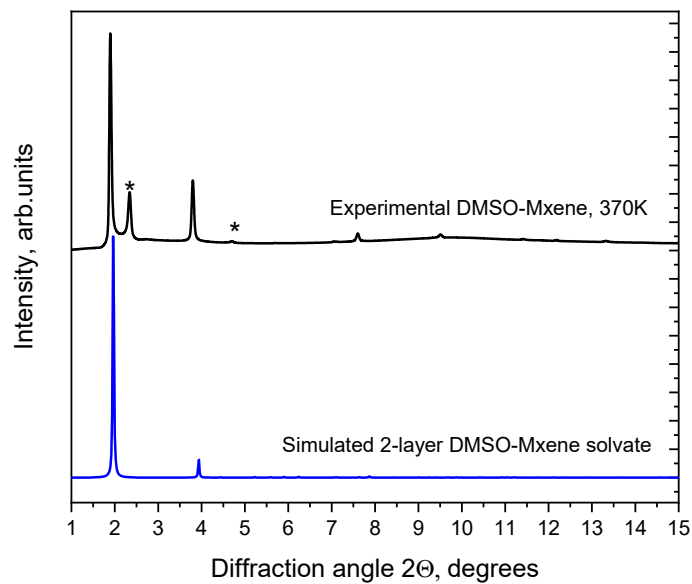


Figure S6 Experimental and modelled XRD diffraction patterns of : a) 1-layered DMSO-Mxene solvate, b) two-layered DMSO-Mxene solvate (remaining peaks from 1-layered solvate are marked by stars)

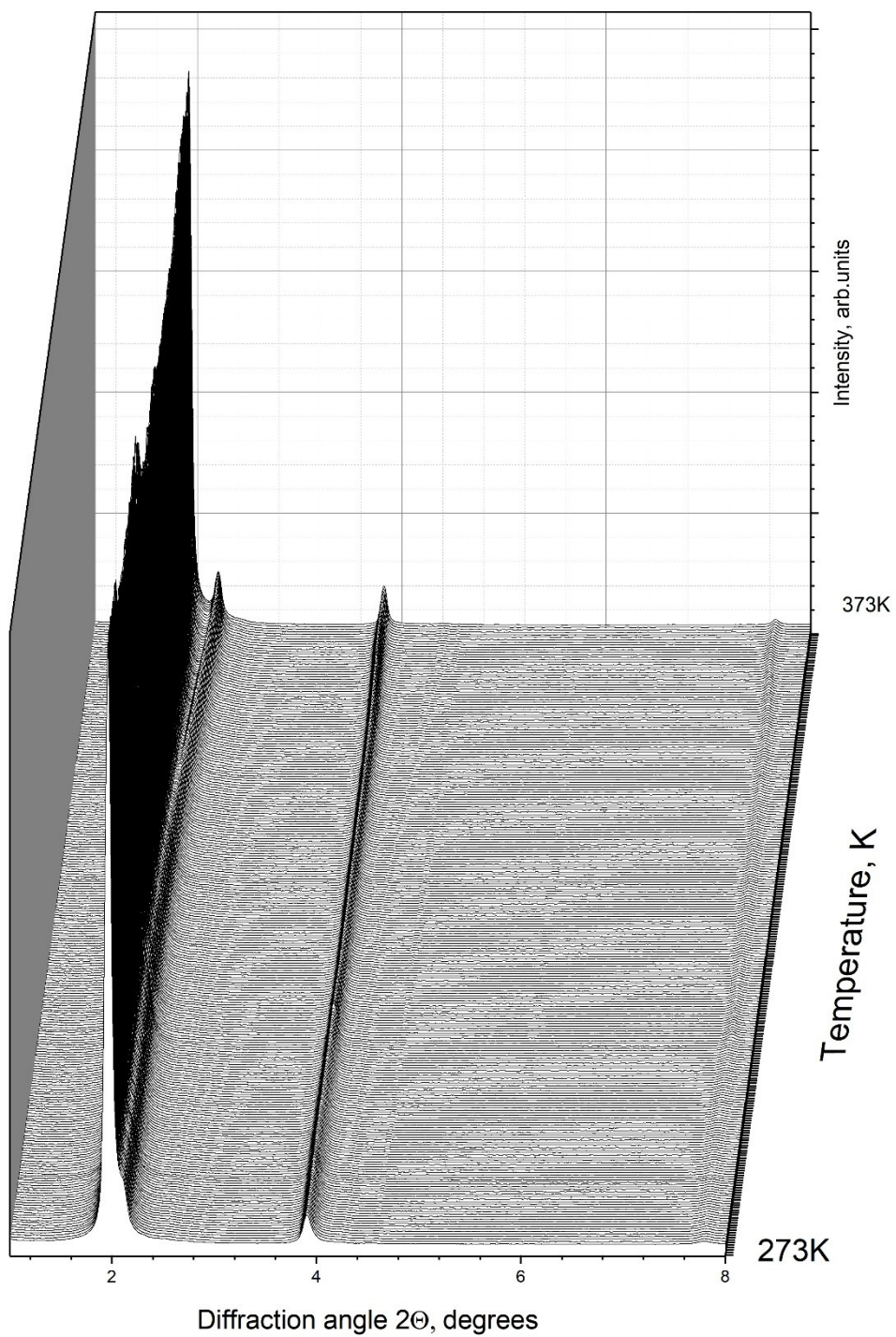


Figure S7 XRD patterns recorded from Mxene 1 sample immersed in in 2:1 H₂O: DMSO mixture upon cooling from 373K to 173K

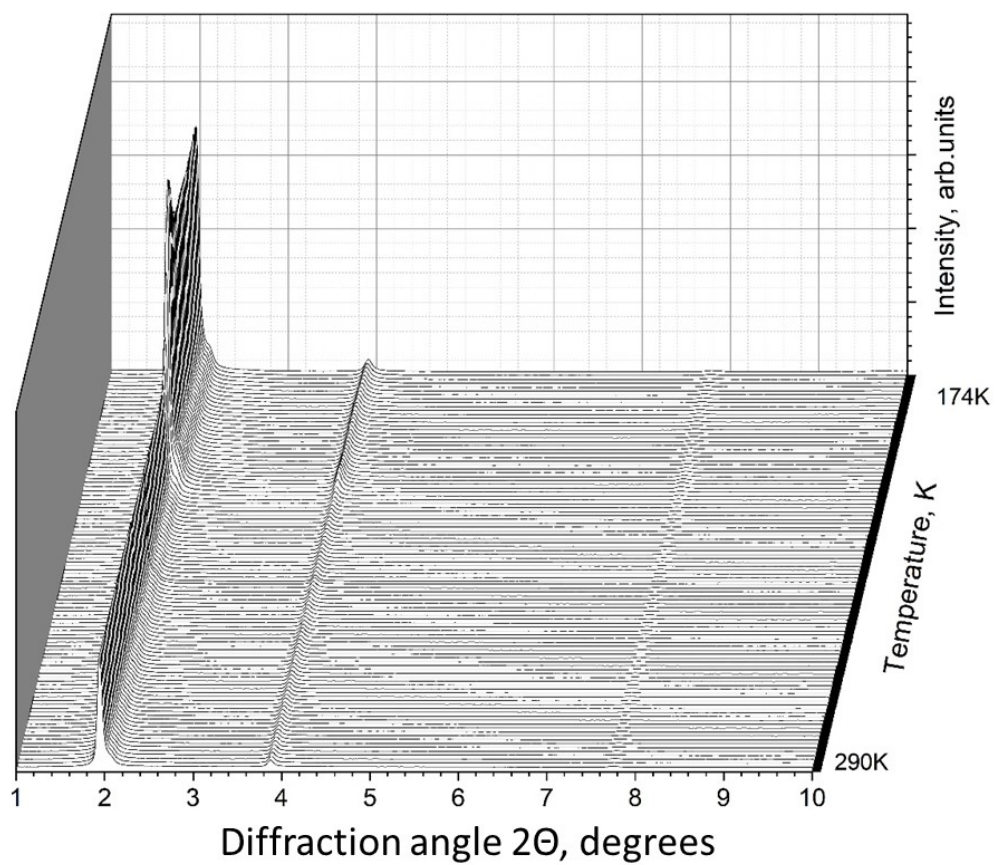


Figure S8 XRD patterns recorded from Mxene 1 sample immersed in in 2:1 H₂O: DMSO mixture upon heating from 174K to 290K. Only 1/3 of recorded patterns is shown for clarity.

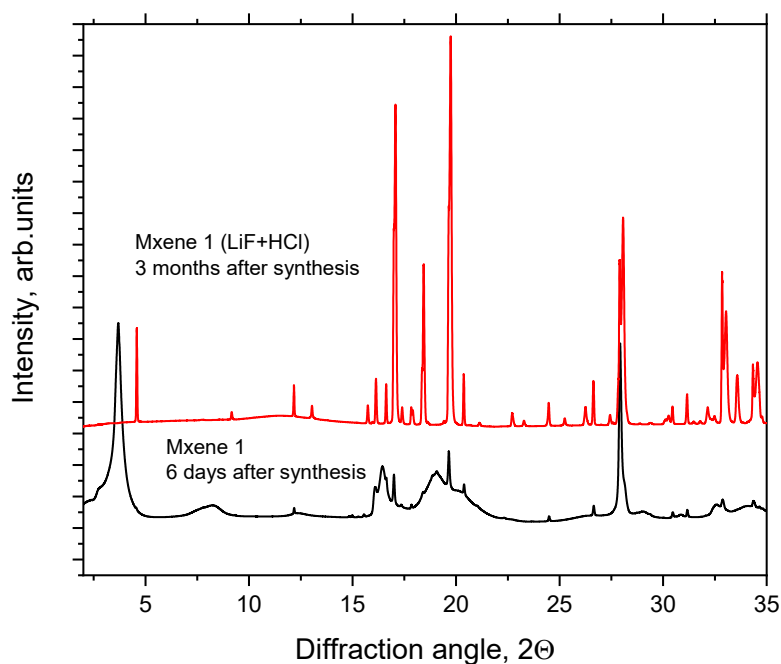


Figure S9 XRD patterns recorded from MXene 1 sample stored in a closed vial for 3 months and from freshly prepared sample (stored 6 days in a closed vial). Complete degradation of MXene 1 during 3 months of storage is obvious as the pattern shows only reflections from titanium oxides. Comparing two patterns shows that weak peaks from titanium oxide are also present in the sample stored for only 6 days and exposed to air for XRD recording.

1. M. Ghidui, J. Halim, S. Kota, D. Bish, Y. Gogotsi and M. W. Barsoum, *Chem Mater*, 2016, **28**, 3507-3514.
2. J. Halim, K. M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen and M. W. Barsoum, *Appl Surf Sci*, 2016, **362**, 406-417.
3. M. Seredych, C. E. Shuck, D. Pinto, M. Alhabeab, E. Precetti, G. Deysher, B. Anasori, N. Kurra and Y. Gogotsi, *Chem Mater*, 2019, **31**, 3324-3332.