

## **Exfoliation, Delamination, and Oxidation Stability of Molten Salt Etched Nb<sub>2</sub>CT<sub>z</sub> MXene Nanosheets**

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## **Supporting Information**

**Methods:**

*Synthesis of Nb<sub>2</sub>AlC MAX Phase:* Elemental powders of Nb (Alfa Aesar, -325 mesh, 99.8%), Al (Alfa Aesar, -325 mesh, 99.5%), and flake graphite (Alfa Aesar, 7-10 micron, 99%) were mixed with the molar ratio of 2.0:1.1:0.95. Due to the low melting point of Al (660 °C) compared to the dwell temperature, the extra Al was added to compensate for the loss during sintering, and the amount of C was adjusted correspondingly. The powder mixture was then ball-milled with ZrO<sub>2</sub> beads in a plastic bottle for 24 hr. at 300 rpm. The mixture was then transferred into an alumina boat and sintered in a tube furnace (GSL-1600X, MTI, CA) at 1600 °C with a heating rate of 5 °C/min for 4 hours under ultra-high purity Ar. The as-sintered sample was drilled and sieved into powders with particle sizes between 20-45 μm.

*Synthesis of Nb<sub>2</sub>CT<sub>z</sub> MXene Nanosheets:* Nb<sub>2</sub>AlC and tin (II) fluoride salt (SnF<sub>2</sub>, Acros Organics) were combined in a 1:6 molar ratio and ground together using a mortar and pestle to obtain a uniform particle size. This powder was then transferred to an alumina boat and loaded into a tube furnace (Thermo Scientific, Lindberg Blue). Etching time ranged from 6-36 hours at 750 °C with a constant circulatory flow of Ar. The Nb<sub>2</sub>CT<sub>z</sub> MXene clay was then added to a 0.1 M potassium hydroxide solution (KOH, Sigma-Aldrich) and allowed to stir at room temperature for 2 hr. (~400-600 rpm). After KOH washing, the solution was poured into 50 mL polypropylene tubes (Falcon REF 352098) for centrifugation at 9,000 rpm for 20 minutes (Beckman Coulter centrifuge). Next, the supernatant was discarded, and the sediment was redispersed in DI H<sub>2</sub>O and centrifuged for 20 minutes at 9,000 rpm. Following this, the supernatant was discarded, and the sediment was dispersed in a 1:4 ratio of water: isopropyl amine (i-PrA) in an enclosed jar for 20 hr of intercalation at room temperature (~400-450 rpm). 1 ml of aqueous dispersion of i-PrA was used for about 60 mg of Nb<sub>2</sub>CT<sub>z</sub> clay for intercalation. After intercalation was complete, the washing process was repeated 4 times via centrifugation. The resultant sediment was redispersed with DI H<sub>2</sub>O and bath sonicated (Fisher Scientific Ultrasonic Bath) for 1 hour in a sealed jar. Lastly, the dispersion was centrifuged at 3,500 rpm for 1 hour. The resulting supernatant of MXene nanosheets was freeze-dried for 24 hours to perform further analysis.

*Dispersions for Oxidation study:* The obtained dispersion after the final centrifugation step was diluted with DI water to get a conc. of about 0.057 mg/ml. The diluted dispersion was kept in a glass vial at room temperature during the oxidation study. The dispersion was used for UV-Vis measurements over a period of 300 hr. to observe the change in absorbance of dispersion.

*Modeling:* The following equation was used to fit the experimental data and quantify the oxidative stability of each of the samples<sup>1</sup>.

$$A = A_0 + A_1 \exp(-t/\tau)$$

where A is the absorbance,  $A_0$  and  $A_1$  are the constants, t is the storage time, and  $\tau$  is the reaction timescale. The ratio of  $A_1$  to  $A_0 + A_1$  indicates the fraction of the sample that is prone to oxidation. The standard error for the model fitting constants was calculated in MATLAB using a 95% confidence interval.

## Characterization

*Scanning Electron Microscopy (SEM):* The morphologies of Nb<sub>2</sub>CT<sub>z</sub> clay and nanosheets were observed with an FEI Quanta 600 field-emission scanning electron microscope. For imaging, the vigorously mixed dispersions of MXenes were freeze-dried for 24 hr. The acceleration voltage used in the imaging was 5 kV. The SEM samples were prepared by drop-casting the diluted dispersion of Nb<sub>2</sub>CT<sub>z</sub> on a silicon wafer and letting it dry under a vacuum overnight.

*X-ray Diffraction (XRD):* XRD patterns of dried Nb<sub>2</sub>CT<sub>z</sub> were obtained using Bruker D8 powder X-ray diffractometer fitted with LynxEye detector, in a Bragg Brentano geometry with a CuK $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation source. The XRD was performed with a step size of  $0.02^\circ$  and a scan rate of 1.5 s per step. The Nb<sub>2</sub>CT<sub>z</sub> samples were freeze-dried before the XRD. A zero-background sample holder was used in all the tests.

*Energy Dispersive Spectroscopy (EDS):* Elemental composition analysis was done using an Oxford EDS detector on FEI Quanta 600 SEM, and results were analyzed using AZtec software by Oxford Instruments. The powdered sample was exposed to a beam, and imaging was done at 20 kV acceleration voltage.

*Atomic Force Microscopy (AFM):* Nb<sub>2</sub>CT<sub>z</sub> dispersion (0.006 mg/ml) was again diluted with water and drop-cast on a freshly cleaved mica substrate. The mica substrate was allowed to dry overnight in a vacuum oven at 30°C. The samples were imaged using Bruker Dimension Icon AFM for scanning probe microscopy, and height profiles were obtained with a MultiMode™ scanning probe microscope.

*UV-Vis Spectroscopy:* UV–Vis measurements were done using Shimadzu UV–vis 2550. The sample used for UV-Vis absorption spectra was a Nb<sub>2</sub>CT<sub>z</sub> dispersion in water with a 0.057 mg/ml concentration. The readings were taken multiple times to achieve maximum accuracy.

*Dynamic Light Scattering (DLS):* The hydrodynamic diameters of aqueous Nb<sub>2</sub>CT<sub>z</sub> nanosheets were determined at ambient temperature by DLS at a scattering angle of 90° using a Zetasizer Nano ZS90 from Malvern Instruments. The colloidal aqueous dispersion of Nb<sub>2</sub>CT<sub>z</sub> nanosheets was diluted to a concentration of around 0.005 mg/mL before making the measurements.

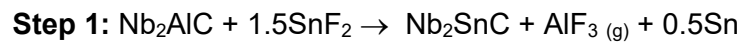
*ζ Potential Measurement:* ζ potential of Nb<sub>2</sub>CT<sub>z</sub> nanosheets in water were measured at ambient temperature using the Zetasizer Nano ZS90 from Malvern Instruments and the appropriate capillary cell, DTS 1070, from Malvern Instruments. To ensure consistency, the Nb<sub>2</sub>CT<sub>z</sub> nanosheets dispersion was diluted to a concentration of around 0.005 mg/mL before measurements.

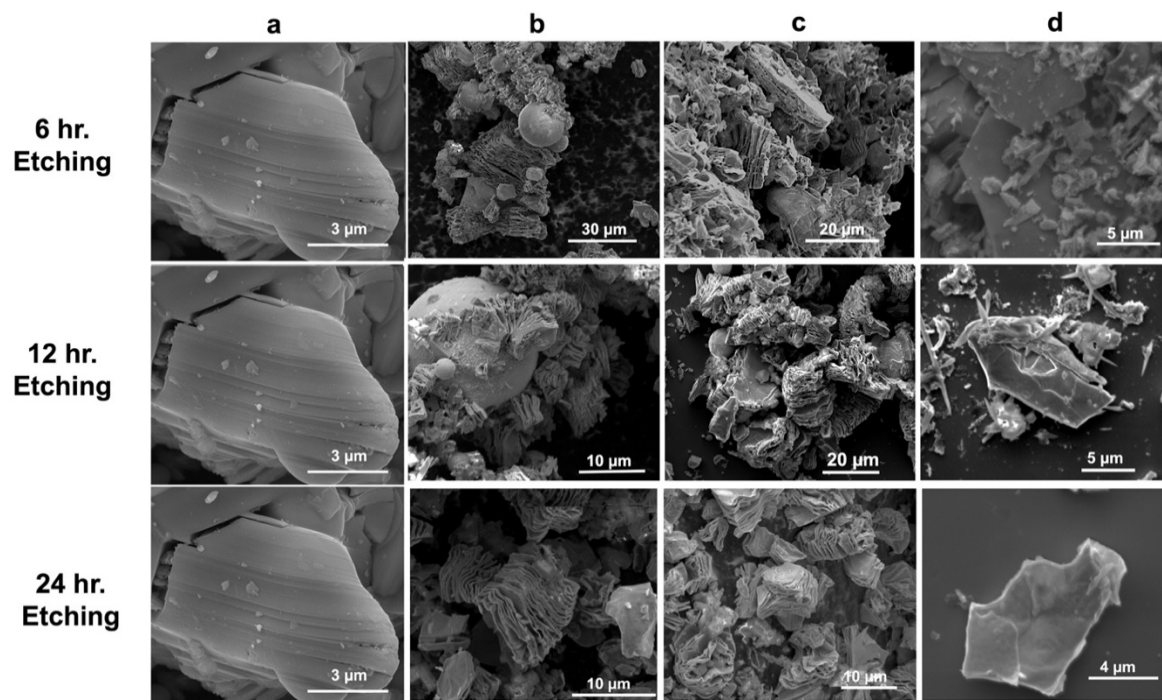
*X-ray Photoelectron Spectroscopy (XPS):* The Samples for XPS analysis (Omicron XPS/UPS system with Argus detector) were prepared by vacuum-assisted filtration (VAF) of the Nb<sub>2</sub>CT<sub>z</sub> MXene nanosheets supernatant. All the samples were vacuum dried for 24 hours prior to XPS measurements. The sample holder for the XPS analysis was cleaned with isopropyl alcohol and dried before measurements. The conducting carbon tape was applied onto a sample holder to place MXene samples for testing. The high-resolution XPS spectra of all the elements were carried out under pass energy of 20 eV and step size of 0.05 eV. The previously reported procedure by Halim *et al.* was used for the deconvolution spectra of Nb 3d, C 1s, O 1s, Sn 3d, and F 1s <sup>2</sup>. The CasaXPS software was used for the component peak fitting. A Shirley-type background function was used to determine background contribution. The adventitious carbon peak (C-C, 284.8 eV) was used for the calibration of all component spectra. Elemental spectra were then separated into the expected components for Nb<sub>2</sub>CT<sub>z</sub> and those are listed in every graph.

The peak fitting was done using a few major constraints. First, all binding energies were constrained to ±0.5 eV of the initial values and allowed to shift in 0.02 eV intervals. All the binding energies were verified with previously reported work. Second, all the full width half maximum values of components were constrained. Finally, Nb components in the Nb 3d spectra were fit using asymmetric peaks with high binding energy tails due to their conducting behavior by earlier reports <sup>2</sup>. Gaussian-Lorentzian curves were used to fit all peaks and components.

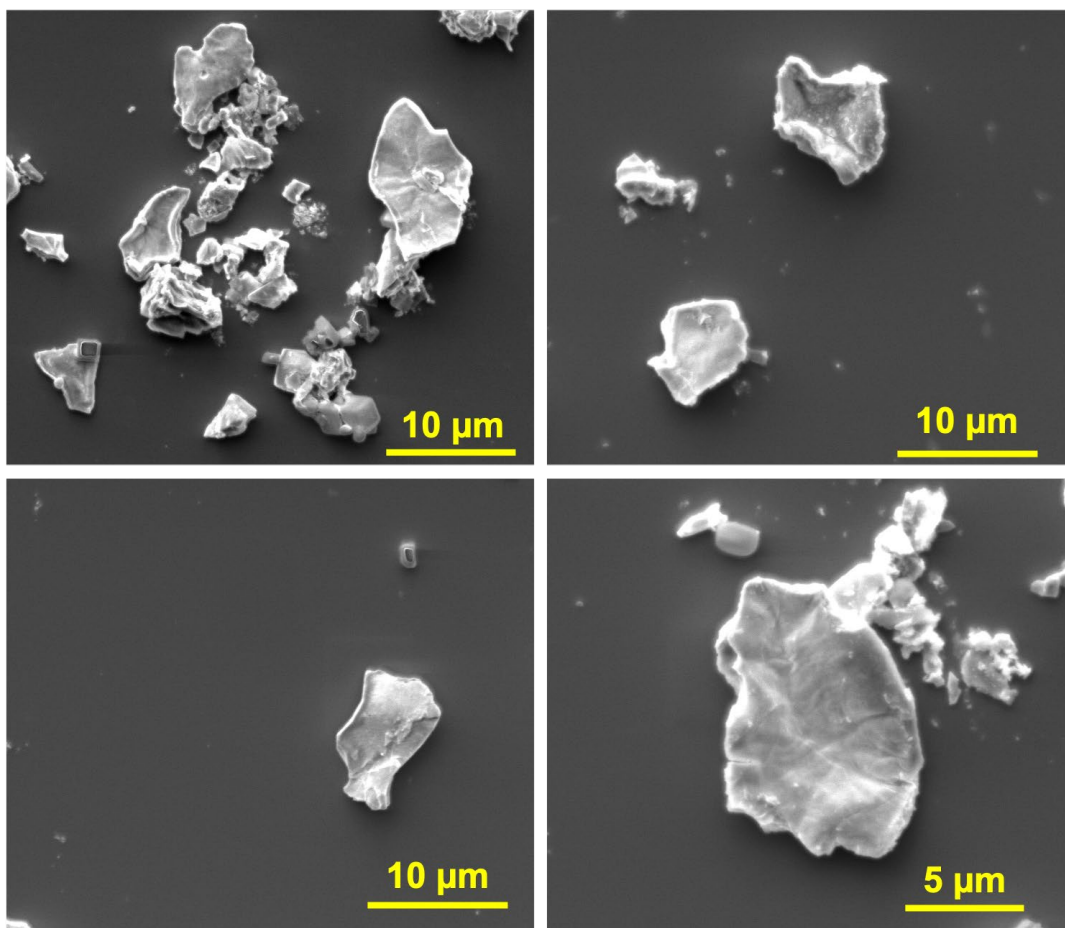
## Section S1:

The earlier work by Li *et al.* has proposed the mechanism for the formation of halide terminated  $Ti_3C_2T_z$  MXene via a molten salt etching approach and we have proposed a similar mechanism in our earlier work on fluorine terminated  $Ti_3C_2T_z$ <sup>3,4</sup>. The formation of F-terminated  $Nb_2CT_z$  via molten salt etching is also a two-step reaction. First, **step 1** involves the replacement of Al in  $Nb_2AlC$  by Sn, which results in the formation of  $Nb_2SnC$ , an intermediate product of  $Nb_2CT_z$ , along with  $AlF_3$  as a by-product is generated. Also, as the reaction proceeds,  $Sn^{2+}$  ions form, which will intercalate into the A site after removing Al from  $Nb_2AlC$ . In **step 2**, the intermediate phase,  $Nb_2SnC$  gains F-terminations in the presence of an excess of  $SnF_2$  salt.





**Figure S1.** SEM images of (a) Nb<sub>2</sub>AlC MAX phase and Nb<sub>2</sub>CT<sub>z</sub> etched for 6, 12, and 24 hr. (b) before and (c) after KOH washing and (d) nanosheet.



**Figure S2.** SEM Images of Nb<sub>2</sub>CT<sub>z</sub> nanosheets etched for 36 hr. (This corresponds to Figure 2d.)



**Table S1.** The elemental composition of Nb<sub>2</sub>CT<sub>z</sub> clay (etched for 6 hr) before and after KOH wash and nanosheets obtained by EDS.

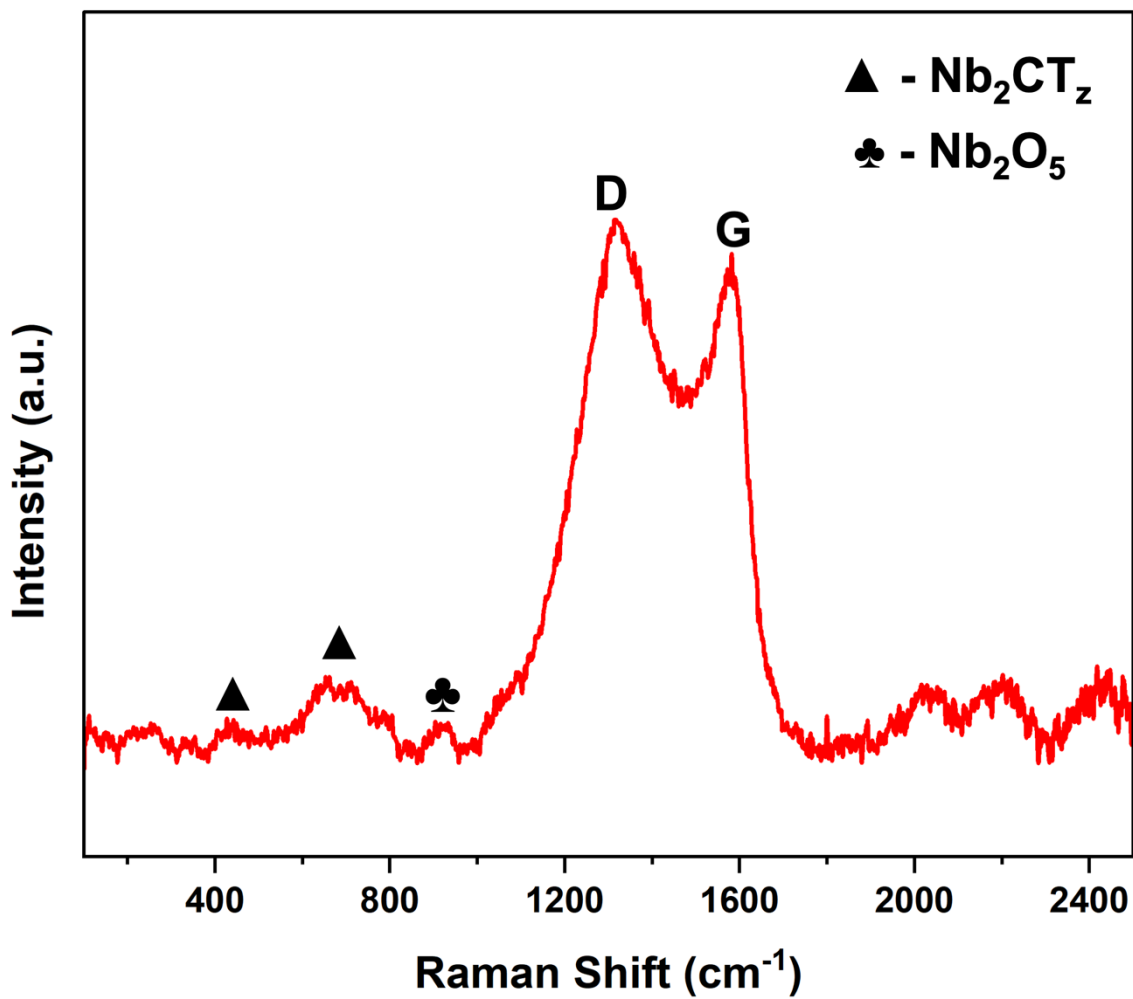
<b>Nb<sub>2</sub>CT<sub>z</sub></b>	<b>Before KOH wash</b>	<b>After KOH wash</b>	<b>Nanosheets</b>
<b>Element</b>	<b>% Weight</b>	<b>% Weight</b>	<b>% Weight</b>
<b>Nb</b>	36.3	17.7	27.8
<b>Sn</b>	11.2	6.0	0
<b>F</b>	21.9	15.7	25.9
<b>O</b>	8.2	12.9	9.8
<b>C</b>	18.4	44.9	29.8
<b>Al</b>	4	2.8	6.7

**Table S2.** The elemental composition of Nb<sub>2</sub>CT<sub>z</sub> clay (12 hr etched) before and after KOH wash and nanosheets obtained by EDS.

<b>Nb<sub>2</sub>CT<sub>z</sub></b>	<b>Before KOH wash</b>	<b>After KOH wash</b>	<b>Nanosheets</b>
<b>Element</b>	<b>% Weight</b>	<b>% Weight</b>	<b>% Weight</b>
<b>Nb</b>	37.1	39	48.5
<b>Sn</b>	12.4	9.7	8.4
<b>F</b>	16.3	12.9	11.7
<b>O</b>	11.3	12	15.1
<b>C</b>	19.5	24.6	14.6
<b>Al</b>	3.4	1.8	1.7

**Table S3.** The elemental composition of Nb<sub>2</sub>CT<sub>z</sub> (24 hr etched) before and after KOH wash and after separation was obtained by EDS.

<b>Nb<sub>2</sub>CT<sub>z</sub></b>	<b>Before KOH wash</b>	<b>After KOH wash</b>	<b>Nanosheets</b>
<b>Element</b>	<b>% Weight</b>	<b>% Weight</b>	<b>% Weight</b>
<b>Nb</b>	33.1	46.4	55.1
<b>Sn</b>	15.8	8.3	5.0
<b>F</b>	24.8	14.9	3.1
<b>O</b>	9.0	11.9	17.9
<b>C</b>	13.2	16	18
<b>Al</b>	4.0	2.5	0.9



**Figure S3.** Raman spectroscopy of Nb<sub>2</sub>CT<sub>z</sub> MXene powder showing characteristic peaks of Nb<sub>2</sub>CT<sub>z</sub>.

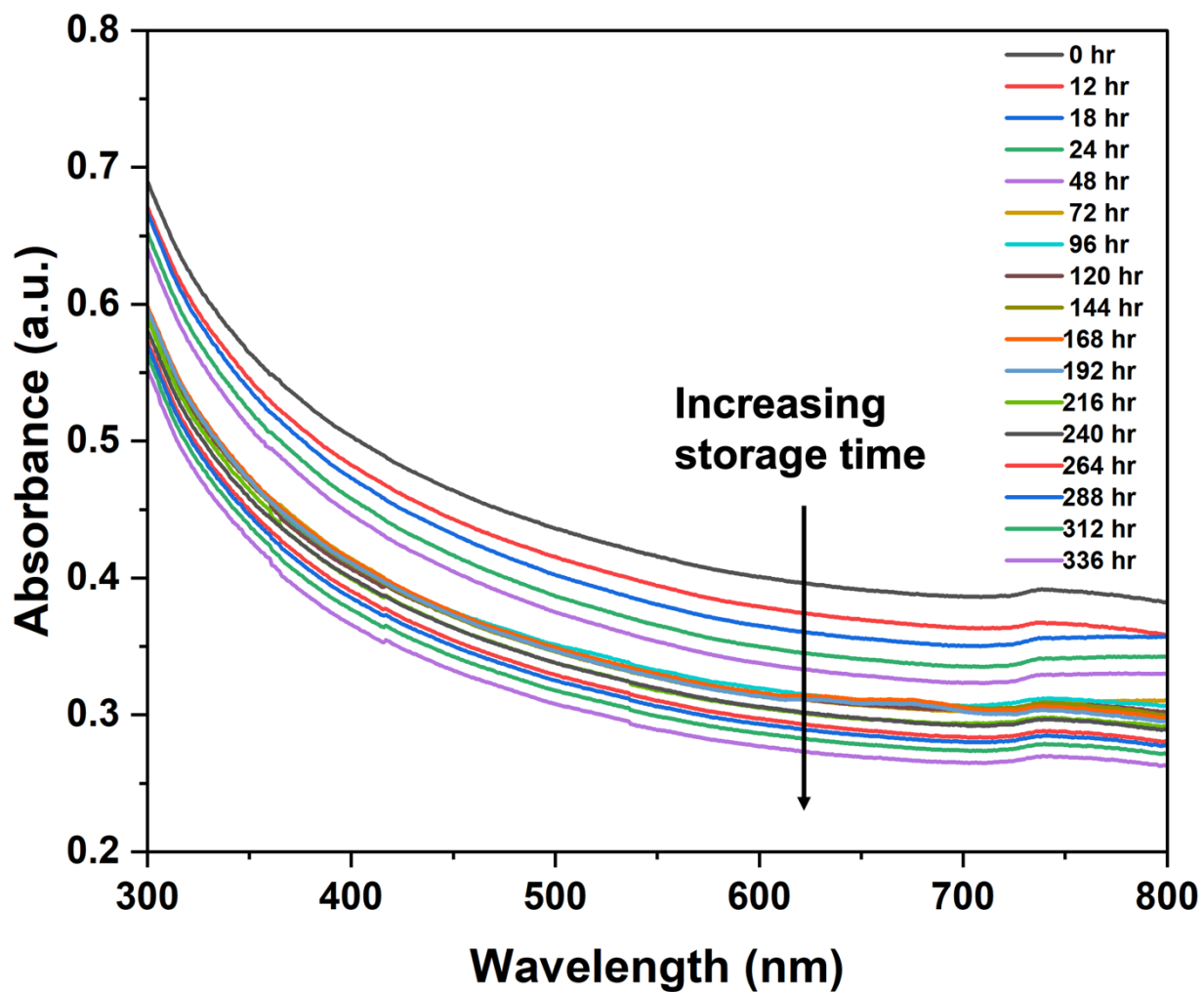
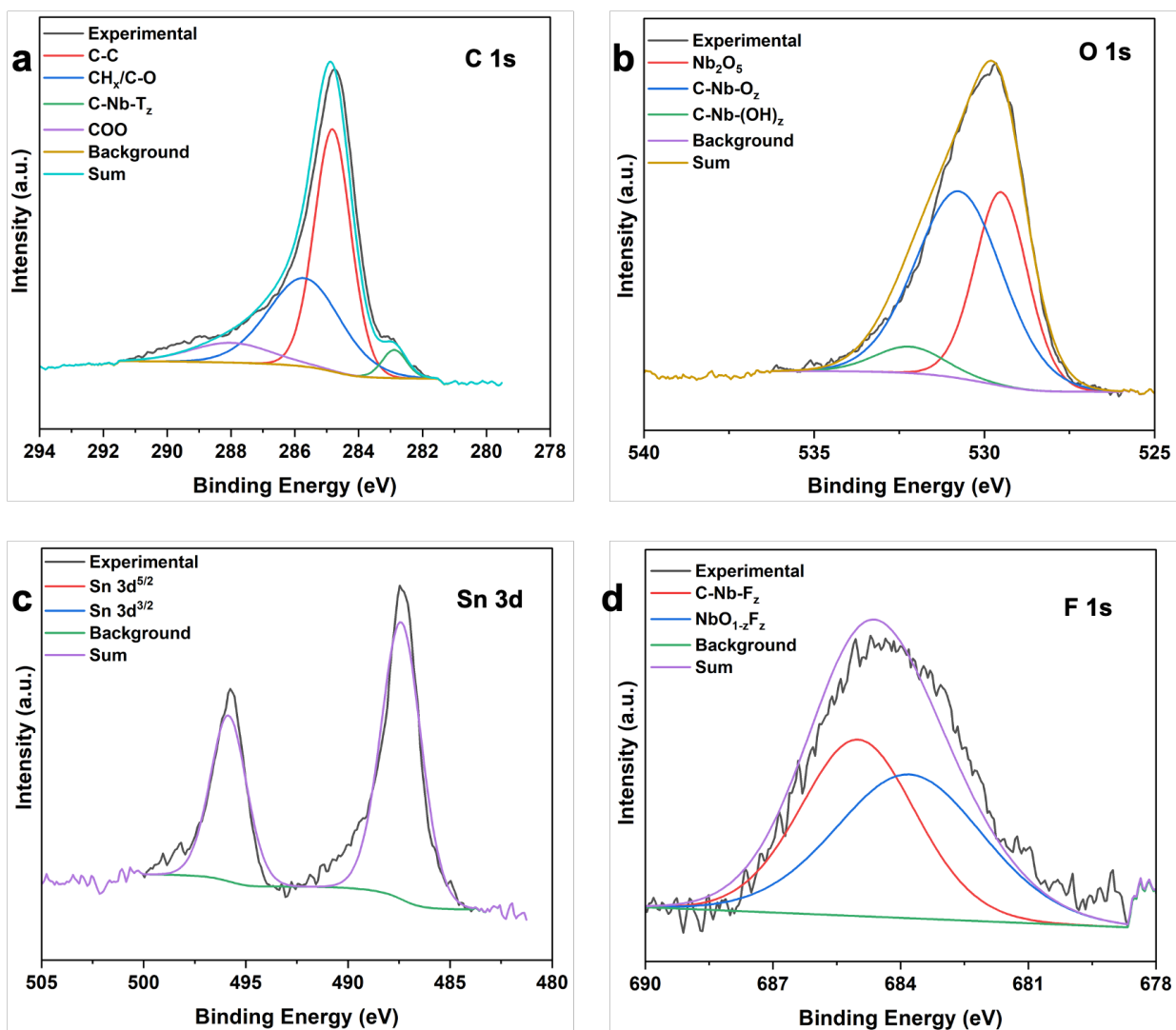


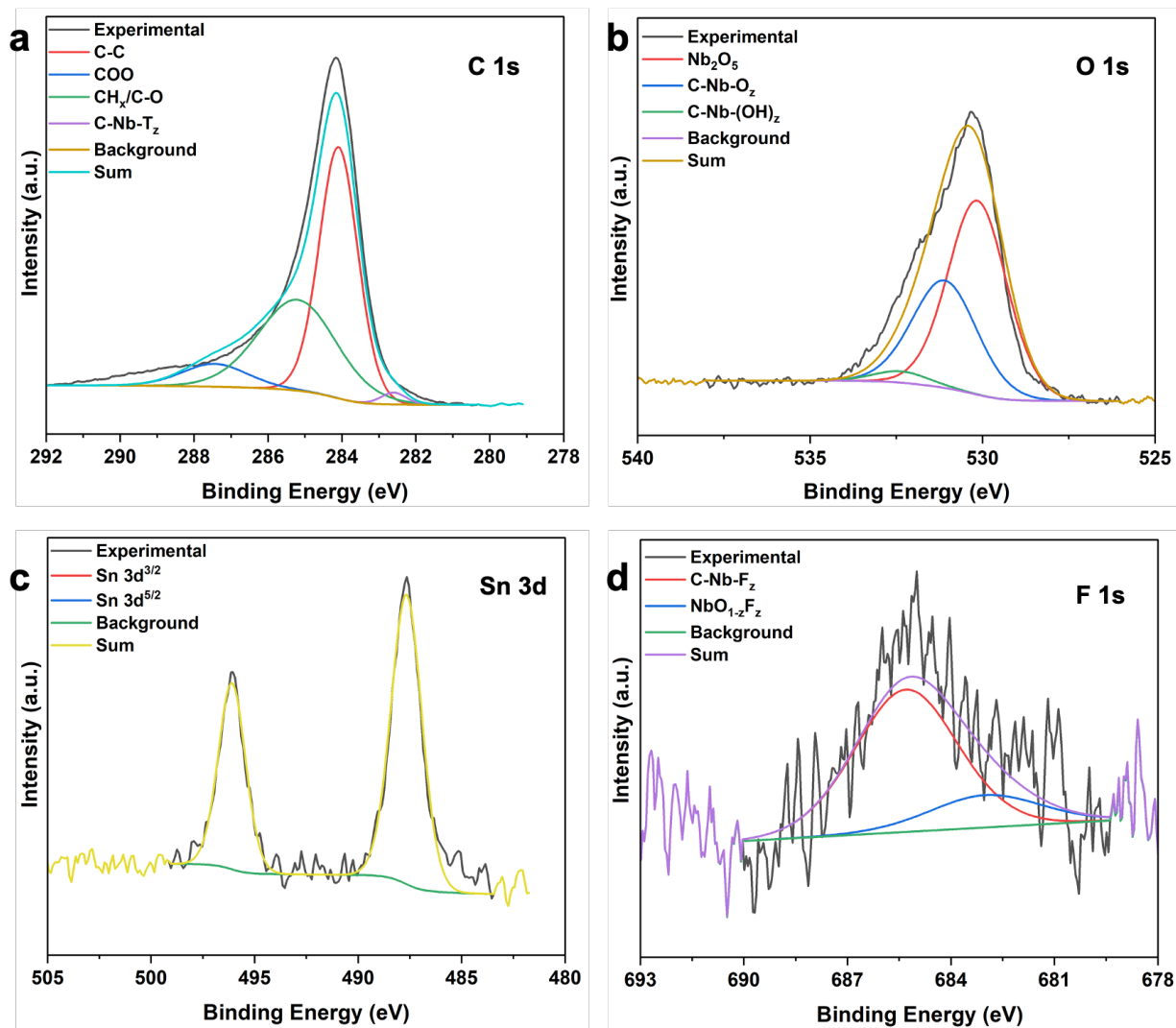
Figure S4. UV-Vis spectra of MXene dispersion at various storage times.



**Figure S5.** The deconvoluted XPS spectra of as-prepared  $\text{Nb}_2\text{CT}_z$  (a) C 1s; (b) O1s; (c) Sn 3d and (d) F 1s

**Table S4.** XPS component peak fitting analysis of as-prepared Nb<sub>2</sub>CT<sub>z</sub> nanosheets

Element	Element at %	Component name	Component at %
<b>Nb 3d</b>	11.67	Nb <sub>2</sub> O <sub>5</sub>	50.03
		NbO	17.29
		Nb <sup>4+</sup> O	5.72
		NbO <sub>1-z</sub> F <sub>z</sub>	4.38
		Nb (I, II, IV)	4.27
		C-Nb-F <sub>z</sub>	18.31
<b>C 1s</b>	51.88	C-C	50.45
		CH <sub>x</sub> /C-O	36.55
		COO	9.07
		C-Nb-F <sub>z</sub>	3.93
<b>F 1s</b>	8.63	NbO <sub>1-z</sub> F <sub>z</sub>	51.07
		C-Nb-F <sub>z</sub>	48.93
<b>O 1s</b>	26.71	Nb <sub>2</sub> O <sub>5</sub>	36.13
		C-Nb-O <sub>z</sub>	57.34
		C-Nb-(OH) <sub>z</sub>	6.53
<b>Sn 3d</b>	1.11	Sn 3d <sub>5/2</sub>	64.66
		Sn 3d <sub>3/2</sub>	35.34



**Figure S6.** The deconvoluted XPS spectra of aged or oxidized Nb<sub>2</sub>CT<sub>z</sub> (a) C 1s; (b) O1s; (c) Sn 3d and (d) F 1s



**Table S5.** XPS component peak fitting analysis of 300 hr. aged Nb<sub>2</sub>CT<sub>z</sub> nanosheets

Element	Element at %	Component name	Component at %
<b>Nb 3d</b>	6.05	Nb <sub>2</sub> O <sub>5</sub>	62.24
		NbO	7.87
		Nb <sup>4+</sup> O	25.75
		Nb (I, II, IV)	4.14
<b>C 1s</b>	78.31	C-C	52.14
		CH <sub>x</sub> /C-O	38.26
		COO	8.01
		C-Nb-F <sub>z</sub>	1.59
<b>F 1s</b>	0.69	NbO <sub>1-z</sub> F <sub>z</sub>	80.19
		C-Nb-F <sub>z</sub>	19.81
<b>O 1s</b>	14.30	Nb <sub>2</sub> O <sub>5</sub>	60.10
		C-Nb-O <sub>z</sub>	36.62
		C-Nb-(OH) <sub>z</sub>	3.28
<b>Sn 3d</b>	0.65	Sn 3d <sub>5/2</sub>	60.88
		Sn 3d <sub>3/2</sub>	39.12

- References:** (1) Zhang, C. J.; Pinilla, S.; McEvoy, N.; Cullen, C. P.; Anasori, B.; Long, E.; Park, S.-H.; Seral-Ascaso, A.; Shmeliov, A.; Krishnan, D. Oxidation stability of colloidal two-dimensional titanium carbides (MXenes). *Chemistry of Materials* **2017**, *29*, 4848-4856.
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