

# Freeze-casting of Ti<sub>3</sub>C<sub>2</sub> MXene suspension

Date: 2021-08-31

Tags: Training Freeze-cast 18/08/2021 Synth Nanoplexus 400 2021

Created by: James Bird

1 / 6

Goal : Freeze-cast Ti<sub>3</sub>C<sub>2</sub>T<sub>z</sub> aqueous nanoparticle suspensions to give well-aligned nanoparticles in a sample within the target dimensions and tolerances

Procedure :

- Add necessary quantity of lyophilizer beakers (Labconco) to ultra-low temperature freezer at - 81 °C and note room temperature
- MXene synthesised in [\[Experiment\] MXene synthesis VII](#) is speed-mixed with the protocol below, to give a smooth, homogeneous paste with no signs of oxidation

Spin rate / rpm	500	1000	1500	2250	3000
Time / s	30	30	30	60	60

- Assemble template using Vaseline jelly to seal joints and to adhere to aluminium top-plate
- Ensure excess Vaseline is removed with a clean cotton bud
- Pour homogenous suspension into a section of the template (smallest cavity dimensions 15x15x21.5 mm), flatten with a spatula and place atop the freeze-plate
- Set target temperature on liquid nitrogen/water flow controller with a ramp rate of - 5 K/min
- Allow uni-directional freezing to complete, so that the freeze-front has visibly reached the entire sample surface
- Don waterproof cryo gloves
- Remove a lyophilizer beaker from freezer
- Remove top-plate with the attached template, deconstruct the frame and remove the sample
- Add sample to beaker and return to freezer - remove cryo gloves
- Set target temperature to room temperature on flow controller with a ramp rate of +10 K/min

The above procedure is repeated, with thorough cleaning of the template and top-plate after each sample is made. Cleaning is carried out with deionised water and

# Freeze-casting of Ti<sub>3</sub>C<sub>2</sub> MXene suspension

**Date:** 2021-08-31

**Tags:** Training Freeze-cast 18/08/2021Synth Nanoplexus 400 2021

**Created by:** James Bird

2 / 6

isopropanol-soaked disposal paper towel, in that order. Three samples are produced, with initial suspension concentrations of 14.83, 4.46 and 2.92 wt%, produced via serial dilution with deionised water and speed-mixing as before. Once all samples have been made, they are attached to the lyophilizer in their beakers.

## Results :

All details of the specific freeze-casting/ice-templating parameters that differed across each sample are summarised below:

Sample / #	Concentration / wt%	Rest time before T ramp / min	Plate temperature at ramp commence / °C	Vaseline applied?	Time from 0 °C to sample frozen / min	Target temperature / °C	Frozen by target temperature?
1	14.83	0	16.1	Y	3	-50	Y
2	4.46	5	17.1	Y	12	-50	N
3	2.92	5	3.8	N	n/a	-70	N

The column 'rest time before T ramp' corresponds to the amount of the time the suspension is allowed to settle before the temperature ramp program is initiated, which can help the suspension surface to become level and hence give a more uniform sample shape. 'Plate temperature at ramp commence' is the temperature that the freeze-plate has acquired before commencing a new temperature ramp for a sample. 'Vaseline applied' corresponds to whether Vaseline was used to seal the template joints ('Y') or not ('N'): in the case where Vaseline was not used, a leak from the underside of the frame was noted, which quickly stemmed itself. 'Time from 0 °C to sample frozen' corresponds to the rough amount of time it took for a sample to completely freeze, after the 0 °C threshold was surpassed. 'Target temperature' is the target temperature set on the flow controller. 'Frozen by target temperature?' corresponds to whether the whole of the structure was frozen, as visible from the surface, by the time the target temperature is reached. The target temperature can be reduced further to ensure the whole of the sample is frozen while subject to a constant temperature ramp.

# Freeze-casting of Ti<sub>3</sub>C<sub>2</sub> MXene suspension

Date: 2021-08-31

Tags: Training Freeze-cast 18/08/2021Synth Nanoplexus 400 2021

Created by: James Bird

3 / 6

Attached .JPEG files are photographs of the samples at various points, as detailed here:

- IMG\_1355-57 show Sample #1 prior to freeze-casting, hence the suspension held in the template atop the top plate
- IMG\_1361 shows Sample #3 prior to freeze-casting
- IMG\_1363 is Sample #3 post-freeze, still retained in the template
- IMG\_1415 is Sample #1 once lyophilized
- IMG\_1417-1419 is Sample #2 once lyophilized, and imaged from various orientations, where the surface that sat directly atop the freeze-plate is the same surface on which the sample sits
- IMG\_1420-22 is Sample #3 once lyophilized. Sample orientation is the same as described above for Sample #2 in images 1421 & 1422. In IMG\_1420 the sample face on the benchtop is one of the smallest, ~ 15 x 15 mm surfaces parallel to the temperature gradient during freezing

Details of the lyophilized samples are summarised in the table below, where 'dim.' is an abbreviation for 'dimension':

Sample / #	Length (long dim. // to freeze-plate) / mm	Width (short dim. // to freeze-plate) / mm	Height (⊥ to freeze-plate) / mm	Volume / cm <sup>3</sup>	Mass / mg	Density / g cm <sup>-3</sup>
1	21.5	15.1	10.2	3.311	382.1	0.115
2	21.5	14.9	15.0	4.805	219.5	4.57 x 10 <sup>-2</sup>
3	21.4	15.1	19.0	6.140	182.9	2.98 x 10 <sup>-2</sup>

Note that the surface of Sample #1 is not flat, and Sample #3 is domed, so dimensions, volumes and densities are rough. Some nanomaterial transfer to the benchtop is visible in photographs of Samples 2 & 3: there is a notable decrease in sample integrity with decreasing concentration, as samples soften at lower densities. Samples 2 & 3 were liable to material transfer, while Sample 1 was not.

# Freeze-casting of Ti<sub>3</sub>C<sub>2</sub> MXene suspension

Date: 2021-08-31

Tags: Training Freeze-cast 18/08/2021 Synth Nanoplexus 400 2021

Created by: James Bird

4 / 6

## Conclusions :

- Vaseline should always be used to seal joints
- Five minutes rest time for the suspension is sufficient to flatten the suspension surface in the template
- Ramp target temperature should be set lower than -70 °C for a 19 mm sample height, and lower than - 50 °C for 15 mm sample height

## Attached files

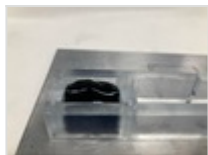
IMG\_1355.JPEG

sha256: f5e61efefac7076080db619a4095ce8c5222faba2db101cc66e3d97e9eec8536



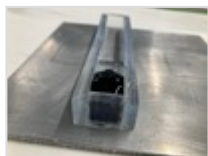
IMG\_1356.JPEG

sha256: 61293d917933dbb407a260cd8ffbf9235355dd0d044057d2f18a9da91b136a14



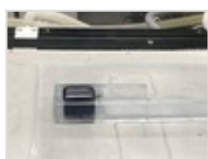
IMG\_1357.JPEG

sha256: b4acbe4824bc4b62bcb7041af5ddebdf5a0e0b5aeaed4a9a75ffb01751d7985c



IMG\_1363.JPEG

sha256: d0dcbee6d4809e2dd7fe939747f6df38daae6ac4d217bcdac0837fd515e290bf



# Freeze-casting of Ti<sub>3</sub>C<sub>2</sub> MXene suspension

Date: 2021-08-31

Tags: Training Freeze-cast 18/08/2021 Synth Nanoplexus 400 2021

Created by: James Bird

5 / 6

IMG\_1415.JPEG

sha256: c71fc222ae2d6a3640f35e63352809031798247d144af82958ec61b56b236a41



IMG\_1417.JPEG

sha256: 850852f176ecb0245ad92bf7c8b6105a8aadd9d7078f595bbb1c36536f48db70



IMG\_1418.JPEG

sha256: 74cc472b9179f82f8fb4338eccc6f2d8291bbf404e87354b2b2e4242faceea0



IMG\_1419.JPEG

sha256: a0de7e12f06f12f9eba7662eb6ebd48988d813a833ee1889dd44cc0e19ee1ecf



IMG\_1420.JPEG

sha256: 21b0b5148b750f8868f2647d7bdc04b8c37028ecb26154a0ecf51ef7ff3f7f62



IMG\_1421.JPEG

# Freeze-casting of Ti<sub>3</sub>C<sub>2</sub> MXene suspension

**Date:** 2021-08-31

**Tags:** Training Freeze-cast 18/08/2021 Synth Nanoplexus 400 2021

**Created by:** James Bird

6 / 6

sha256: 75e176885efbad07a96a74c404fee16fb9d17eb855a9f661902159d9841b7e7f



IMG\_1422.JPEG

sha256: f2a15c4fbcc51bc07458f9089d774415ff26bfba8d3f1b0a4776a9e32fcc0839



IMG\_1361.JPEG

sha256: 2c009c17f7459089198075bc2f11164220bcba5c2c7de670a1ff60bbe9e3f47d



Unique eLabID: 20230310-64e1913ad21328990617e8fa89489aaedf6f3a72

Link: <https://frankel-elab.manchester.ac.uk/experiments.php?mode=view&id=91>