

Raman spectroscopy of free-standing MXene film

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

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Goal :

Find optimal operation parameters for Raman spectroscopy in order to verify the composition of freeze-cast and compressed $\text{Ti}_3\text{C}_2\text{T}_z$ films

Procedure :

- One of the samples which was freeze-cast ([Experiment - Freeze-casting of \$\text{Ti}_3\text{C}_2\$ MXene suspension](#)), lyophilized and calendared ([Experiment - Calendering of freeze-cast MXene aerogel](#) or [Experiment - Calendering of freeze-cast MXene aerogel II](#)) is placed atop a glass microscope slide using tweezers, then sealed in the Raman spectroscope beneath the objective lens.
 - Which sample exactly was used cannot be tracked, although both were freeze-cast from the same synthesis product, and should differ only in thickness, density and initial freeze-cast concentration.
- Renishaw inVia Reflex Raman Spectroscopy instrument is calibrated with internal silicon standard and 785 nm IR laser wavelength
- Raman spectra are captured repeatedly whilst changing various parameters including magnification, pinhole use, laser intensity, degree of confocality, scan type (extended or static), accumulation count and exposure time.

Results :

Only the 'best' spectra (i.e. those captured with presumed-optimised parameters) were saved and exported, with filenames as detailed here:

- BestComparison_###x.txt and .wxd files, where the hashtags are replaced with the objective lens magnification used, contain the Raman spectroscopic data where .txt versions are two-column data of Raman shift and intensity, whilst .wxd files are the raw WiRE-legibile datafiles.
- 50x_Best_.jpg are optical images through the microscope at 50 x magnification,

where is either '1before' or '2after' to indicate whether the image was captured before or after laser irradiation.

All the 'best' spectra were captured twice, where the filenames system altered slightly for the second version (v2), such that:

- BestComparison_###xv2.txt and .wxd files are much as described before.
- ###x_Bestv2_.jpg where hashtags are replaced with the objective lens magnification used and is as before.
- Each of the v2 images described above also have a corresponding ###x_Bestv2_3subtract.png, where the hashtags are as before. This image is the subtraction of '1before' from '2after' performed in ImageJ.

The 'best' settings were determined experimentally to be those given in the table below, where the key factors considered are signal-to-noise ratio (SNR), recorded counts (intensity), sample scorching and overall time to record a spectra. Laser power measured at the sample (without objective) is measured to be 151.8 mW, and 237 mW at the source.

Magnification / x	Laser Power / %	Pinhole	Confocality	Exposure / s	Accumulations	Type
20	100	In	Standard	10	3	Extended
50	10	Out	Standard	10	3	Extended
100	10	Out	Standard	10	3	Extended

Image files Raman785_Bestv#_Ti3C2_FC_Training.png, where # is either 1 or 2, are plots of the Raman spectra at using each available magnification lens (20, 50 and 100 x), using the 'best' collection parameters for the first and second runthrough, v1 and v2, respectively. Plots are producing using Python script Raman_FindPeaks.py, available on Github at <https://github.com/jamesbird58/ThesisMethods>. Some peak locations on each plot are identified and annotated.

Conclusions :

The 20x magnification most consistently displays the expected Raman modes, including the $A_{1g}(C)$ mode at $\sim 720 \text{ cm}^{-1}$, albeit with low SNR and with some degree of shifting. Each vibration mode identified in T. Hu et al., Phys. Chem. Chem. Phys.

17, 9997 (2015) can be correlated with the identified peaks in the 20x magnification v2 spectrum as detailed in the table below.

Mode	Raman shift in Ref. A. Sarycheva and Y. Gogotsi, Chem. Mater, 2020 / cm^{-1}	Observed Raman shift / cm^{-1}
ω_1	123	154
ω_2	202	202
ω_3	720	722
ω_4	620	624
ω_5	286	280
ω_7	361	371

- 'Best' conditions still led to scorching (see ###x_Bestv2_3subtract.png images) and possible measurement of 'bare' MXene, as demonstrated from shifts in observed Raman shifts.
- The laser power should be reduced to $\leq 10\%$ for all objectives in order to achieve a target range of 0.5-1mW (0.3-0.7% of full laser intensity)
- Accumulations should be increased to five with 60 s exposure to improve SNR
- Must map a larger region to avoid effects of roughness (100 points in 10 x 10 μm region in streamline mode).
- Collection up to 1800 cm^{-1} enables checking for graphitic carbon
- Photoluminescence from TiO_2 oxidation product could be giving a large background. Measurements can be repeated with fresher material, as these samples are nearly 3 month old sample.

Attached files

BestComparison_20x_go.txt
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BestComparison_20x_go.wxd
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BestComparison_50x.txt
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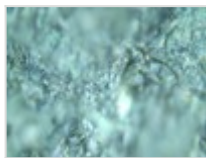
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50x_Best_1before.jpg

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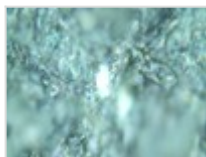


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50x_Best_2after.jpg

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100x_Bestv2_2after.jpg

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100x_Bestv2_1before.jpg

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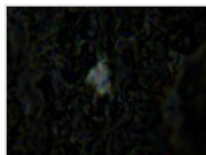


BestComparison_20xv2.txt

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100x_Bestv2_3subtract.png

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BestComparison_20xv2.wxd

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BestComparison_50xv2.txt

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BestComparison_50xv2.wxd

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BestComparison_100xv2.wxd

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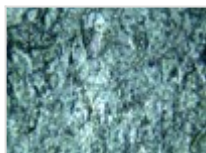
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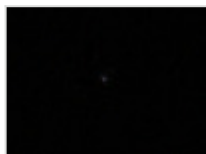
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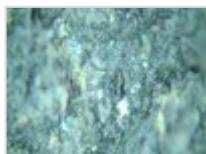
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50x_Bestv2_1before.jpg

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50x_Bestv2_2after.jpg

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50x_Bestv2_3subtract.png

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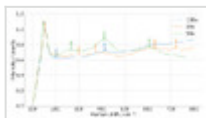


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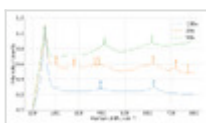
Raman785_Bestv1_Ti3C2_FC_Training.png

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Raman785_Bestv2_Ti3C2_FC_Training.png

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Link: <https://frankel-elab.manchester.ac.uk/experiments.php?mode=view&id=124>