

# Dynamic Light Scattering (DLS) for nanoparticle size-distribution acquisition V

Date: 2021-09-29

Tags: PSD DLS 18/08/2021 Synth Nanoplexus 400 2021 LCC

Created by: James Bird

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Goal : Obtain particle size distributions (PSDs) of LCC-fractionated  $\text{Ti}_3\text{C}_2$  MXene nanoparticles in aqueous suspension using DLS

Procedure :

## Sample preparation

- $\text{Ti}_3\text{C}_2$  product suspension synthesised in [\[Experiment\] MXene synthesis VII](#) is diluted to 2.99 wt% in [\[Experiment\] Freeze-casting of  \$\text{Ti}\_3\text{C}\_2\$  MXene suspension](#) (also see [\[Experiment\] Vacuum-filtration of MXene nanoparticle suspension](#) for concentration validation) and then fractionated using liquid cascade centrifugation in [\[Experiment\] Liquid Cascade Centrifugation \(LCC\) of MXene nanoparticle suspension to reduce PDI in DLS](#)
- Fractionated suspensions are further diluted as necessary for DLS, as detailed in [\[Experiment\] Liquid Cascade Centrifugation \(LCC\) of MXene nanoparticle suspension to reduce PDI in DLS](#)
- Suspensions are homogenised throughout with vortex mixing (Velp Scientifica, ZX3 Advanced Vortex Mixer)
- Final suspensions are transferred to the DLS measurement cuvette with a disposable Pasteur pipette, and the cuvette exterior gently dried if necessary

Samples were unfortunately stored for six weeks prior to measurement since the synthesis was begun, so despite degassing samples with inert gas, sealing with parafilm and storing under refrigeration, some oxidation will likely have occurred. Furthermore, a day prior to this experiment, the fridge where the samples are stored was found off, and it may have been for a total of 8 days, encouraging yet more oxidation from the higher temperatures. After turning the fridge back on, the temperature setting had been adjusted so the samples measured here were found frozen on the following day (the day of the measurements). To accelerate sample thawing, all vials containing suspensions were placed on a hotplate at 50 °C until no ice visibly remained. Samples freezing at these low concentrations is likely to have resulted in nanoparticle coalescence, which further reduces the reliability of PSDs.

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## DLS operation

Standard Operating Procedure (SOP) settings (size measurement type):

- Narrow band filter fitted
- Material properties (RI = 1.7, absorption = 0.9)
- Water dispersant ( $\eta$  = 0.8872 cP, RI = 1.330)
- Use dispersant viscosity as sample viscosity
- Temperature = 25 °C with 120 s equilibration time
- DTS1070 folded capillary cell *only*
- 173 ° backscatter measurement angle
- Automatic measurement duration
- Three measurements per sample
- Automatic attenuation selection and positioning method seeking optimum
- General purpose (normal resolution) analysis model *only*

## Results :

All measurement outputs and variables indicative of data quality are detailed in the table below. All individual measurements returned a polydispersity index (PDI) > 0.1, which defines the threshold below which outputs can only be compared quantitatively. For no single sample, did all three individual measurements meet the data quality criteria defined in the analysis program (Zetasizer) : although for one sample all data quality indicators were met on average, so all the indicators and the Z-average have been highlighted green in those rows (Fraction 4 <  $\eta$  / krpm  $\leq$  5).

Fraction sedimented under rotation speed of $\eta$ / krpm	Concentration / wt %	Z-average / d.nm	Z-average std / d.nm	Number mean / d.nm	Number mean std	PDI / dimensionless	PDI std	Derived mean count rate / kcps	Derived mean count rate std	Intercept	Intercept std	In range / %	In range std
< 1.5	$1.3 \times 10^{-2}$	1205	9	533	415.9	0.517	0.072	219.1	18.4	0.898	0.0168	83.5	3.2
< 1.5	$1.6 \times 10^{-4}$	759.2	301.8	183.6	11.38	0.696	0.181	214	10.1	0.308	0.0471	69.4	9.92

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1.5 < $\square$ 2	$1.6 \times 10^{-2}$	2899	80.47	1531	1117	0.305	0.061	5698.9	110.6	0.948	0.0108	89.8	0.954
1.5 < $\square$ 2	$2.6 \times 10^{-4}$	386.3	71	136.3	22.47	0.426	0.098	80.5	2	0.264	0.0314	82.9	3.48
2 < $\square$ 3	$7.8 \times 10^{-3}$	354.4	66.4	59.92	11.42	0.418	0.06	172.3	5.4	0.392	0.0304	86.9	1.82
2 < $\square$ 3	$1.3 \times 10^{-4}$	352.6	29.81	168.5	21.09	0.583	0.159	226.5	16.3	0.416	0.0282	90.4	0.404
3 < $\square$ 4	0.11	396.5	71.15	97.62	69.97	0.547	0.250	70.4	11.2	0.471	0.0323	77.8	6.56
4 < $\square$ 5	$5.7 \times 10^{-3}$	202.2	36.19	65.74	21.97	0.375	0.018	455.8	18.6	0.926	0.0292	93.4	2.5
> 5	$1.5 \times 10^{-3}$	647.5	136.7	98.82	34.99	0.602	0.026	208.2	47.9	0.524	0.0577	83.3	1.25

The yellow-highlighted Z-average values correspond to samples where three of the four quality indicator variables are in a suitable range across all measurements, such that the value can be deemed reasonably accurate. Common to the intensity PSDs of green and yellow-highlighted samples is a sharp drop-off in density at the larger end of the particle dimension scale: this corresponds to a poor distribution fit to the correlogram on longer timescales, corresponding to those larger particle dimensions which extend beyond the measurement capability of the software under these conditions.

.dts is the raw datafile which can be read into the Zetasizer software program, .csv is an exported, comma-separated summary of the .dts datafile and .png files are the plotted data; particle diameter (on a log scale) is plotted against the mean percentage of that diameter interval contributing to the intensity-based and number-based particle size distribution for each concentration, labelled iPSD and nPSD, respectively. Plotted data correspond to values in the table below, where certain measurements have been rejected on the basis of not sufficiently meeting data quality criteria (DQC) (i.e. < 3 criteria met) and others have been merged when 3 of 4 DQC are met across two measurements of the same sample at different concentrations. Vertical lines spanning the whole plot height are mean Z-average and number mean values (quoted below), where the regions of matching colour spanning left and right of this value correspond to its standard deviation.

Fraction sedimented under rotation speed of $\square$ / krpm	Concentration / wt %	Z-average / d.nm	Z-average std / d.nm	Number mean / d.nm	Number mean std	PDI / dimensionless	PDI std	Derived mean count rate / kcps	Derived mean count rate std	Intercept	Intercept std	In range / %	In range std
< 1.5	$1.3 \times 10^{-2}$	1205	9	533	415.9	0.517	0.072	219.1	18.4	0.898	0.0168	83.5	3.2
1.5 < $\square$ 2	$1.6 \times 10^{-2}$	2899	80.47	1531	1117	0.305	0.061	5698.9	110.6	0.948	0.0108	89.8	0.954
2 < $\square$ 3	nan	353.5	46.04	114.2	61.37	0.501	0.140	199.4	31.6	0.404	0.0295	88.7	2.28
4 < $\square$ 5	$5.7 \times 10^{-3}$	202.2	36.19	65.74	21.97	0.375	0.018	455.8	18.6	0.926	0.0292	93.4	2.5
> 5	$1.5 \times 10^{-3}$	647.5	136.7	98.82	34.99	0.602	0.026	208.2	47.9	0.524	0.0577	83.3	1.25

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Hence, it is found that the Z-average does indeed decrease with increasing centrifugation speed, but only for those fractions sandwiched between two centrifugation speeds. This finding is perhaps not surprising, considering the PDIs of the  $< 1.5$  and  $> 5$  krpm fractions are the highest of the measurements carried forward (i.e. those not ruled out on DQC grounds) in the table listed above, which poses an issue for the fitting algorithm. These upper and lower fractions are presumably indeed the most polydisperse considering they contain all of the smallest and largest nanoparticles.

Comparisons can be drawn with the non-LCC fractionated  $\text{Ti}_3\text{C}_2$  synthesis product from the same synthesis (see [\[Experiment\] Dynamic Light Scattering \(DLS\) for nanoparticle size-distribution acquisition IV](#)). In order to reconstruct PSDs which account for the concentration of each fraction in LCC, the mass of each fraction must be calculated relative to the mass of nanomaterial in the original (bulk) suspension. The table below shows the mass of nanomaterial in each fraction, where concentration and volume calculations are described in [\[Experiment\] Liquid Cascade Centrifugation \(LCC\) of MXene nanoparticle suspension to reduce PDI in DLS](#).

Fraction sedimented under rotation speed of $\omega$ / krpm	Concentration / wt%	Volume / mL	Nanomaterial mass / mg	Mass fraction
Bulk	2.99	5	149.5	nan
$< 1.5$	1.3	3.5	45.5	0.304
$1.5 < \omega < 2$	1.3	3.5	45.5	0.304
$2 < \omega < 3$	0.79	3.5	27.65	0.185
$3 < \omega < 4$	0.11	3.5	3.85	0.026
$4 < \omega < 5$	$5.7 \times 10^{-3}$	3.5	0.20	0.001
$> 5$	$1.5 \times 10^{-3}$	6.5	0.10	0.0007

Using the mass fractions given above, each PSD can be multiplied by its fraction,

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the PSDs summed and scaled to 100%. The  $3 < \eta/\text{krpm} \leq 4$  fraction is again not included due to DLS inaccuracy (DQC not met), meaning  $\sim 2.6\%$  of the distribution has been excluded. The same method is used for the non-LCC fractionated PSDs also. The PSDs are overlay in the plot suffixed LCCComp.png.

## Conclusions:

- Number PSD quantities carry large uncertainties for both LCC and non-LCC measured suspensions, and are deemed unreliable
- The average PDI of 'successful' LCC fractionated suspensions (those not rejected on DQC grounds) is  $0.460 \pm 0.119$ , compared to  $0.322 \pm 0.065$  for successful non-LCC fractions, so polydispersity does not appear to have been reduced.
- 'Extend measurement duration for large particles' option should be selected in Zetasizer software due to sharp drop-off in percentage contribution to PSD at the top end of the particle size range
- Numerous experimental issues plagued LCC reliability, including a lack of proper equipment, accidental freezing of suspensions, probable oxidation due to extended post-synthesis storage and storage inadequacies (refridgeration disturbed)
- In depth comments on the reconstructed PSDs for both non-LCC and LCC suspensions will be spared, although it is likely that the broader derived sum-PSD for the LCC suspension is a better representation of the polydisperse nanoparticle distribution considering the limitations of the fitting algorithm for non-lognormally distributed particle sizes

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## Attached files

2021-09-29.dts

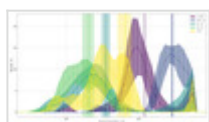
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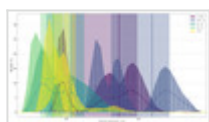
DLS\_2021-09-29\_iPSD.png

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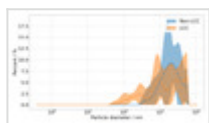
DLS\_2021-09-29\_nPSD.png

sha256: 17212dc01d8e8f0e5ab62dfa10af5e0e9e6c97f41b1cc1faf86de2dff579970f



DLS\_2021-09-29\_LCCComp.png

sha256: 01e11391b889289b1341c3a8871f01766f8c0147134180ddfb480f791261fe38



Unique eLabID: 20230315-2f45efe2db18b769a685fbf7f44e803c55cb6859

Link: <https://frankel-elab.manchester.ac.uk/experiments.php?mode=view&id=98>