

Supporting information for

# In-process monitoring of graphene nanoplatelets production using Raman spectroscopy and NMR relaxation

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## Laser Diffraction

Figure S1 shows additional data from the laser diffraction measurements.

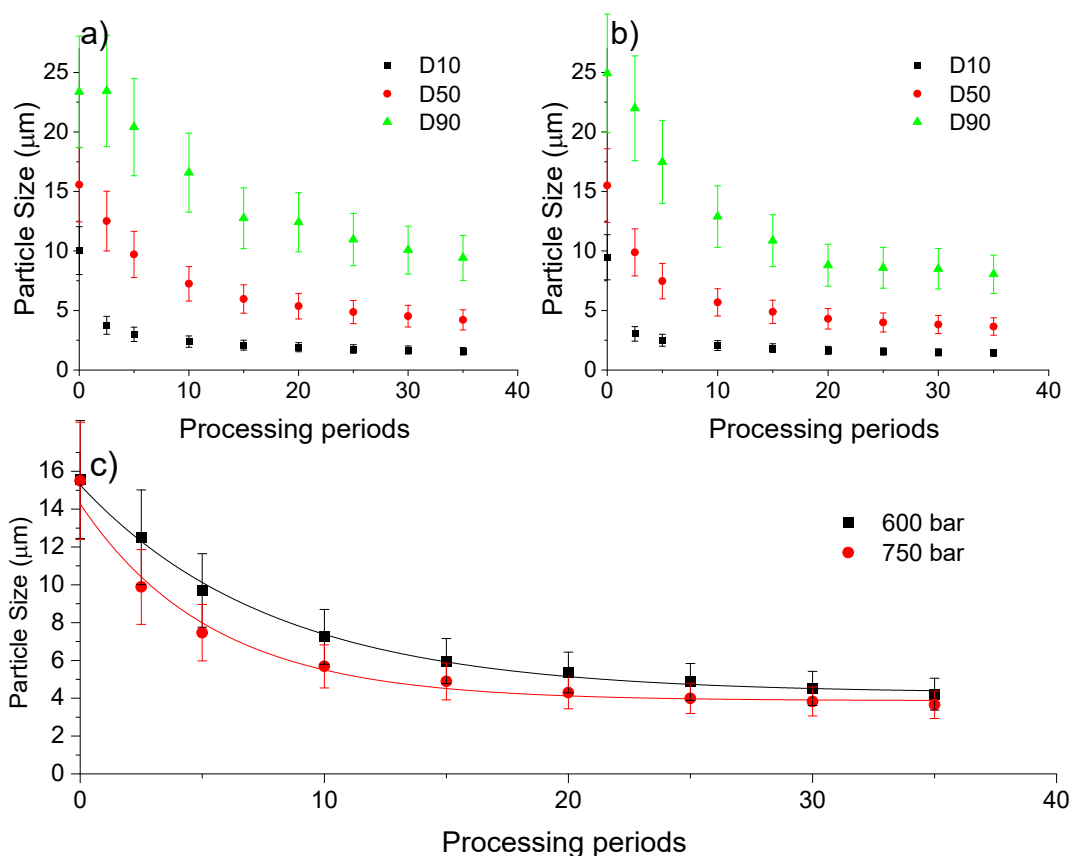


Figure S1: Results of laser diffraction measurements, showing the reported particle size values from the measured distribution, from production using low pressure (a) and high pressure (run C) (b) in the homogeniser head. The median values ( $d_{50}$ ) for both pressures are shown in c). Error bars show an uncertainty of 20% in the values, based on the upper range of deviation found in reference<sup>32</sup>.

## Cascade Centrifugation

Samples of graphene nanoplatelets (GNPs) prepared in *bis*-pyrene stabiliser were size selected using a four-stage cascade centrifuge technique.

In stage 1, the bulk graphite/unexfoliated material was removed by centrifugation at 3500 rpm (904 g) for 20 mins. The supernatant was collected using a pipette and retained, with the sediment then discarded. This step was repeated for a total of three times, centrifuging the supernatant each time, to improve size selection accuracy ensuring as much bulk material is removed as possible.

In stage 2, the final supernatant fraction from stage 1 was centrifuged at 9500 rpm (6659 g) for 30 mins. The supernatant collected using a needle and syringe and centrifuged using the same conditions. The sediment from both steps were combined in DI water to produce the 'large size fraction'.

In stage 3, the retained supernatant from stage 2 was centrifuged at 15,000 rpm (16,603 g) for 60 min. The resulting supernatant was collected via needle and syringe and centrifuged under the same conditions. The sediment from both steps was collected in minimal DI water to give an intermediate fraction, which was not used in this work.

In the final stage, the supernatant from stage 3 was centrifuged at 15,000 rpm (16603 g) for 180 min. The resulting supernatant was collected via needle and syringe and centrifuged under the

same conditions. The sediment from both steps was collected in minimal DI water to give the ‘small size fraction’. This process is summarised in figure S2.

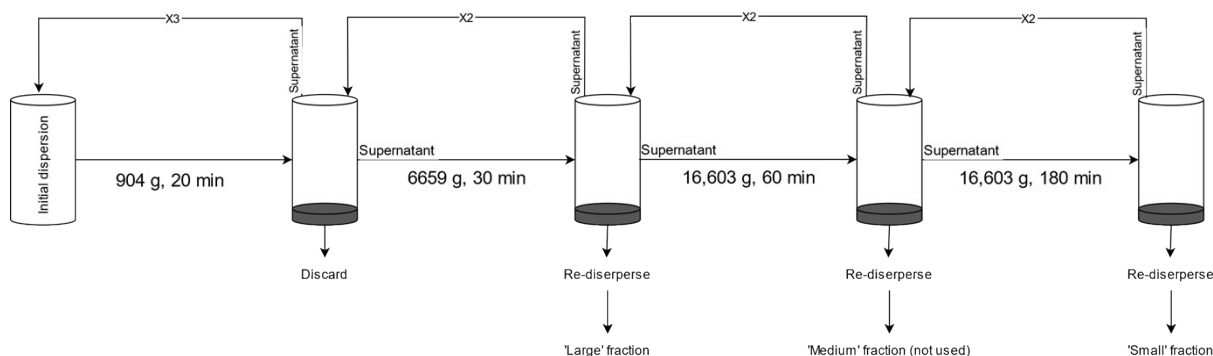


Figure S2: Schematic diagram of cascade centrifugation-based flake size selection process.

## Comparison of $^1\text{H}$ NMR relaxation measurements

$^1\text{H}$  NMR relaxation was used to measure the average T2 relaxation times of the dispersions both at-line and in a temperature-controlled laboratory, as discussed in the Methods section. Slightly lower values of relaxation rates were measured in the laboratory compared to measurements at-line. Figure S3 re-plots figure 3 to highlight the differences.

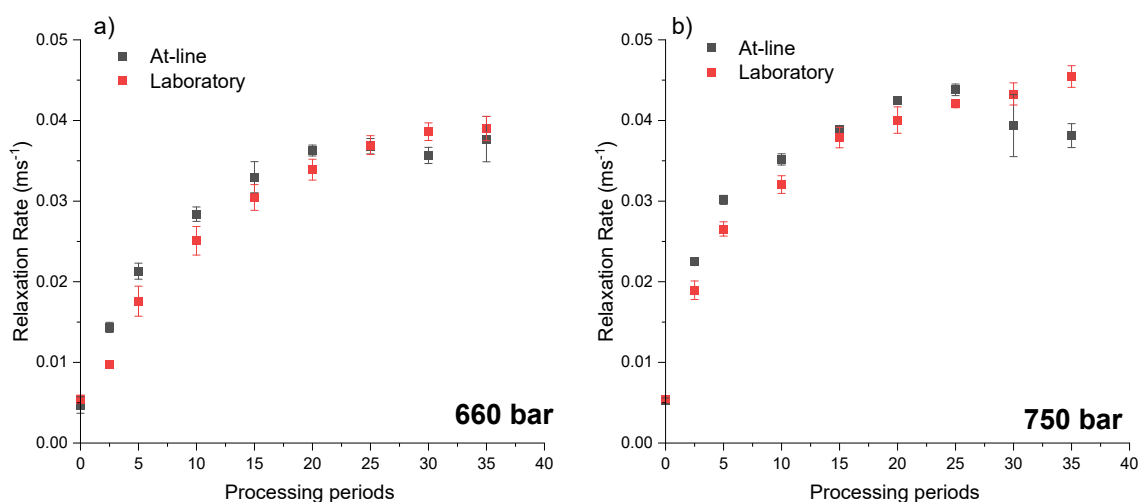


Figure S3:  $^1\text{H}$  NMR relaxation rates vs number of processing periods measured with a homogeniser head pressure of (a) 600 bar and (b) 750 bar. Error bars in the figure represent standard deviations from 3 repeats on the same samples. Fittings were performed employing an exponential decay model (ExpDec2 in OriginLab).

## Measurement of alternative GNP dispersions

To confirm that the instrument used for in-line measurements has sufficient performance to identify changes in flake size of particles directly in a dispersion, a sample was prepared through sonication exfoliation. Centrifugal separation was then used to obtain dispersions with large and small mean lateral sizes, without large unexfoliated material. The flakes in these samples were characterised by AFM and found to have a mean lateral size of  $306 \pm 138$  nm and  $85 \pm 35$  nm respectively. Raman spectra were acquired from these dispersions using the same instrument and settings as for the off-line measurements described above. As shown in figure S3, the spectra obtained from the two

samples are clearly different, with a higher  $I_D/I_G$  ratio obtained from the sample with smaller flake sizes. These size selected samples do not have any large, unexfoliated material present, suggesting these large particles are playing a role in the unexpected behaviour in the Raman results seen from the material system measured in-line.

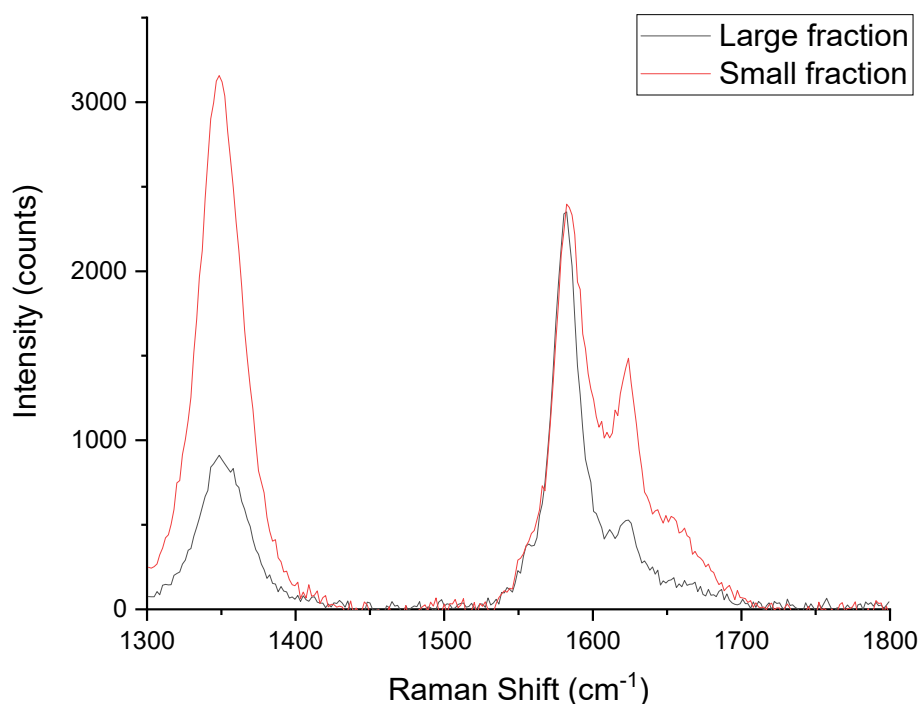


Figure S4: Raman spectra of size selected samples prepared using sonication-assisted exfoliation, measured off-line using same spectrometer used for in-line measurements.

## Laboratory-based Raman spectroscopy measurements

To assess the effect these processes may have on the sample, measurements were made offline, using the same aliquots used for laser scattering and NMR relaxation measurements. These measurements were made without the flow-cell, focussing on the top surface of a static droplet of the dispersion. All samples were measured at room temperature and pressure, and without any bulk flow occurring. As shown in figure S5, the results from these measurements show the same trend as the in-line measurements. This suggests that the unexpected results from the in-line measurements are not the result of measuring the samples in a flowing system. The same aliquots were then filtered through membranes to obtain dry films of GNP flakes, to remove any interfering effects from the water. The fitted results from these spectra are shown in figures S5c and S5d, showing a drop in measured  $I_D/I_G$  ratio after 2.5 processing periods, then little measurable change in value thereafter. The lack of change in the latter stages of the exfoliation is in line with previous reports on the low sensitivity of Raman spectroscopy to identify changes in mixed graphite/FLG systems.<sup>17</sup>

The decrease in  $I_D/I_G$  ratio seen for the samples in dispersion, both in-line and off-line, is unexpected, and is not fully understood. The results from the GR-Py samples suggest that the large, unexfoliated particles are playing a role in these results. We suspect that there is also an effect from the flakes not having an orientation (close to) normal to the incident laser beam, as is found in most studies on the change in  $I_D/I_G$  with lateral flake size. The contribution of the edges of flakes, as opposed to the

edges of the basal plane, will be more significant for larger flakes, and so this effect is not seen in the GR-Py samples where these large particles have been removed. However, further investigations are required to fully understand this causes behind these results.

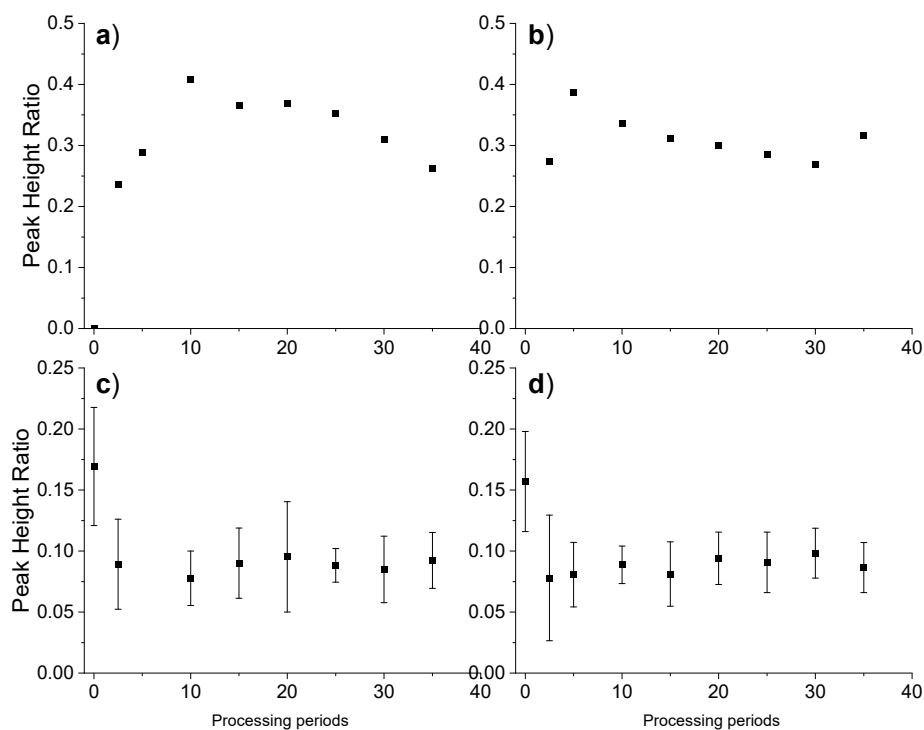
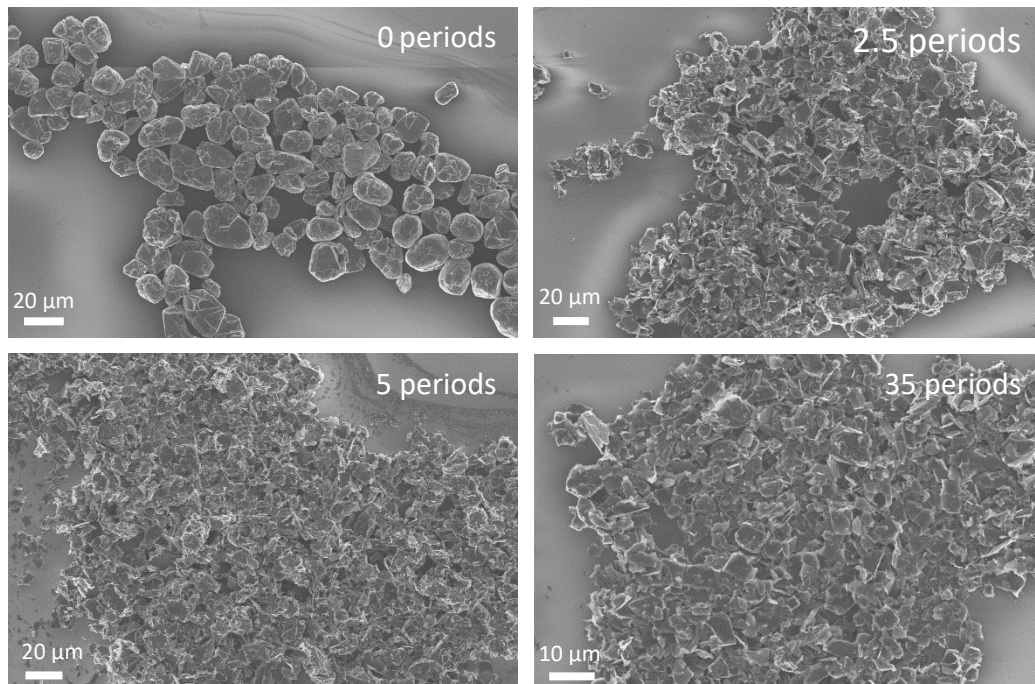


Figure S5: Results of Raman spectroscopy results measured off-line on aliquots taken at specific numbers of processing periods, using the same spectrometer used for in-line measurements (a and b) or a confocal spectrometer on filtered films (c and d). Results are shown for exfoliation at 600 bar (a and c) and 750 bar (b and d).

## Scanning electron microscopy

To understand the changes in morphology of the GNPs during the processing, samples were imaged using scanning electron microscopy. Samples from the aliquots taken for off-line measurements were drop-cast onto silicon wafers (20 nm thermal oxide thickness) heated to 110 °C. Images were acquired on a Zeiss Supra microscope, using 5 kV accelerating voltage and an inLens detector. Figure S6 shows example images, showing a rapid decrease in the particle sizes during the initial few processing cycles, with smaller changes seen after that. This is in agreement with the laser diffraction and NMR measurements, where particle size and surface area show faster changes in the earlier stages of the processing.



*Figure S6: Example SEM micrographs of the particles found in aliquots taken at specific number of processing periods through the reactor.*