

Correlation between size distribution, morphology and chemical analysis of Graphene Family materials

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1. Introduction

Two groups of GFM (graphene family) materials provided by University of Turin (UT) and Haydale Ltd. (HD) were analysed within the ACCORDs project (funded through Horizon Europe) for size distribution with different light scattering methods and morphology/crystallinity/ chemistry of individual flakes/ particles via transmission electron microscopy (TEM) in bright field and diffraction mode.

Comparison of results between imaging techniques and ensemble methods in liquid provides valuable insight into potential mechanisms of biological or environmental toxicity related to different size fractions and individual particle morphologies as well as surface modifications.

2. Materials and Methods

PSD

The Particle Size Distribution (PSD) was measured using a Malvern Panalytical Mastersizer 2000 laser diffraction instrument. The samples were measured in DI water, with a set of five measurements without sonication to assess the pristine PSD followed by 10 measurements with 30 sec US treatment between measurements. Samples were taken as received without any prior treatment. Additional measurements were carried out using Dynamic Light Scattering (DLS) on a Malvern Zetasizer NS instrument and Nano Tracking Analysis on a Malvern Nanosight instrument.

(S)TEM/EDX

TEM samples were prepared by drop casting 10µl of the dispersion (as received) onto 400mesh holey carbon coated copper grids (AgarScientific) and left to dry for at least 1 hour at RT prior to TEM examination. Images and diffraction patterns were obtained on a 200kV analytical JEOL 2100 instrument equipped with an OI EDS detector. Chemical

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composition was assessed with electron dispersive X-ray spectroscopy (EDX) in STEM mode.

3. Results

Particle Size Distribution in liquid

The UT samples show mainly one very broad peak in the range between 1 and 100 μm with some additional small peaks in the several hundred μm range. Sonication can change the mean peak value to either higher or lower values. HD samples as received with no sonication show mainly two peaks: the larger size is in the range of 10-200 μm and a smaller peak between approximately 1 and 10 μm . After sonication an additional peak between approximately 100 and 500nm can be observed. Additional DLA and NTA measurements showed mainly peaks in the 100 to 1000 nm range, larger particles/agglomerates cannot be measured by either of these techniques.

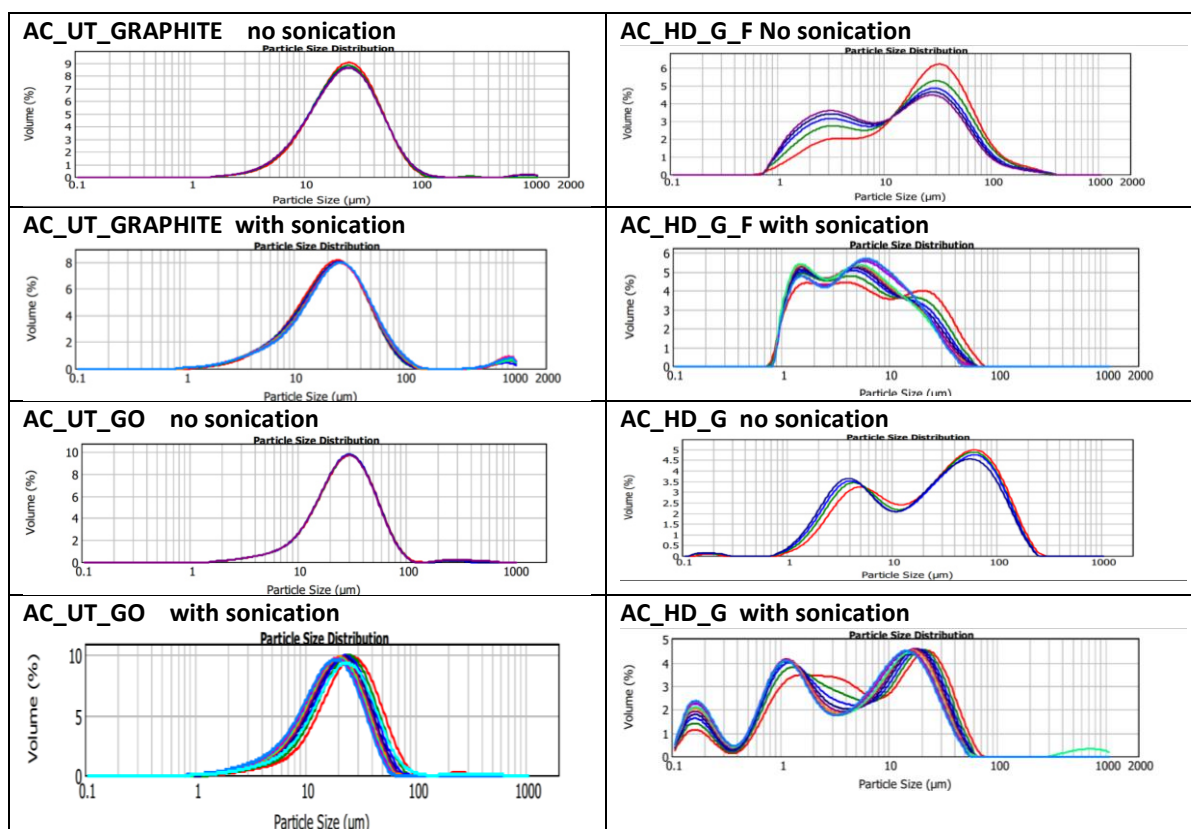


Figure 1: Examples of Particle (Agglomerate/Aggregate) Size distribution of two types of GFM samples with and without sonication

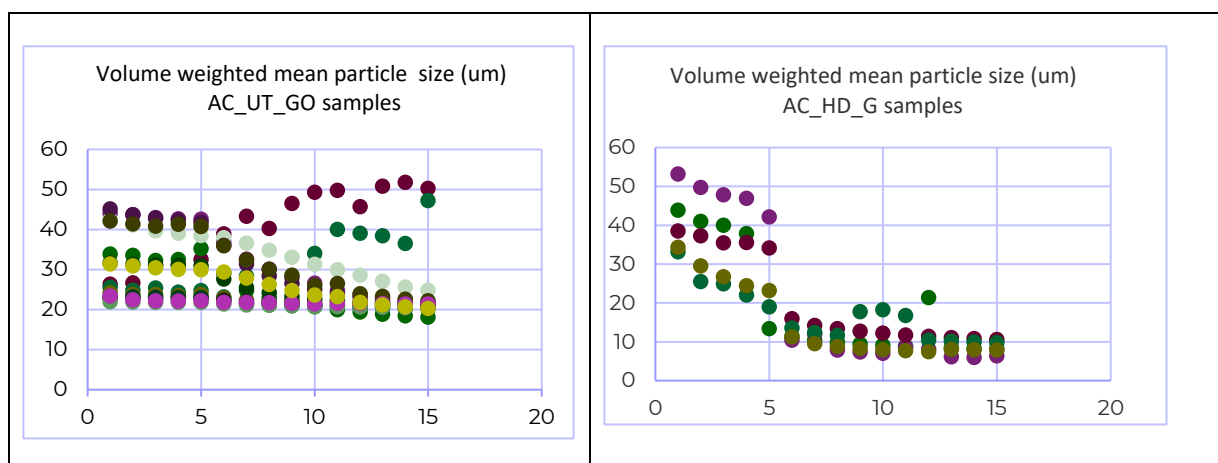


Figure 2: Volume weighted mean particle size change with stirring /pumping (measurement 1-5) and sonication (measurement 6-15)

4. Comparison of PSD in liquid versus imaging methods

The upper limit for particle size measurement in TEM is limited by the size of the TEM grid square (approx. 30 μ m). Overlapping particles as well as the irregular shapes make particle size estimates from TEM images difficult. Drying platelets or sheet like samples onto TEM grids may result in additional changes in perceived shapes. While the UT samples show large individual GFM flakes in the 10-50 μ m range, this size range is mostly associated with agglomerates or aggregates in the HD samples. Both sample groups also show much smaller particles which are primary particles or small agglomerates of GFM materials.

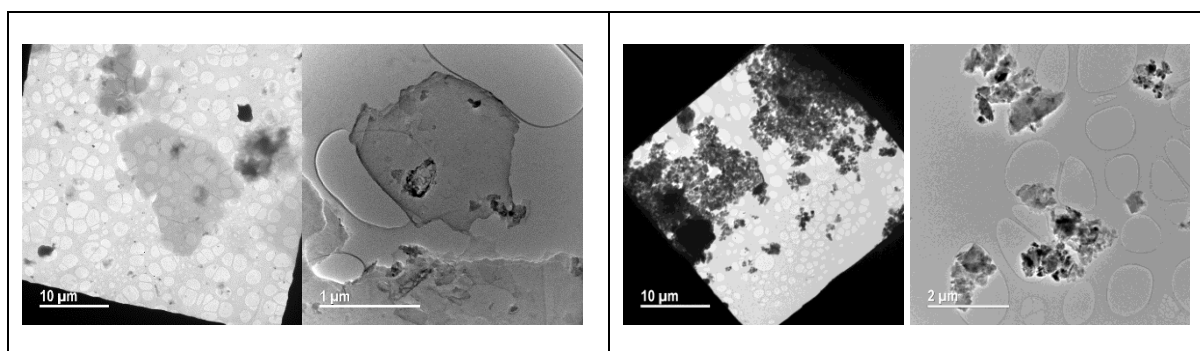


Figure 3: Low and medium magnification images of UT and HD samples

5. Comparison of chemical content (C/O ratio)

EDX maps were acquired from random areas and additional spectra were obtained from areas with no carbon support. Between 10 and 55 spectra were analysed for each sample and spectra where either oxygen or carbon had zero counts were excluded from the analysis. The amount of all additional elements detected was below 2at% in all areas.

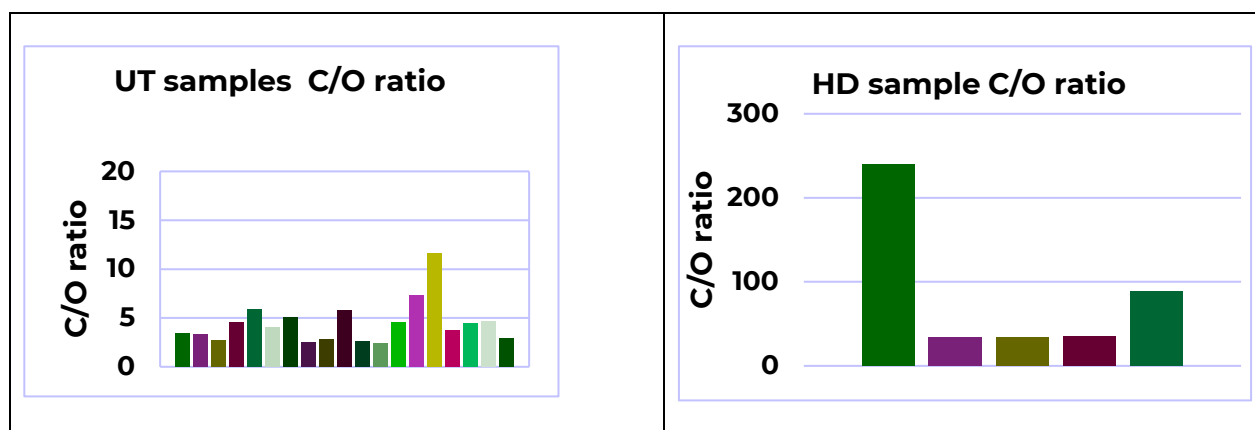


Figure 4: C/O ratios from EDX spectra in STEM mode

While the overall C/O ratio and the amount of impurities/ contamination was in good agreement with other techniques, the standard deviation error for all spectra from each individual sample was high. This indicates either a strong variation of the oxidation degree within each type of GFM material or a variation between different types of GFM as present in each sample. Generally, the HD samples are more homogeneous in terms of morphology and chemical contents, whereas the UT samples show a stronger variation of C/O ratio overall and some correlation between the morphology and chemical contents.

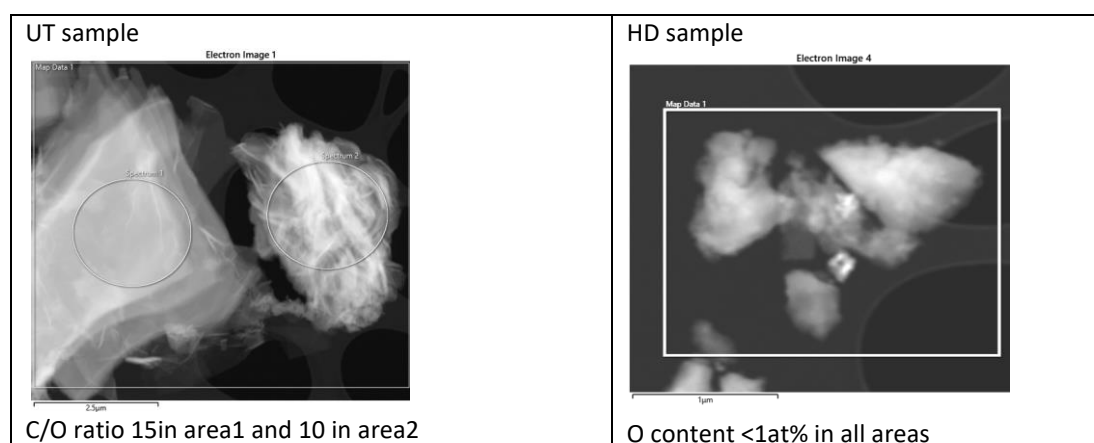


Figure 5: Morphology and C/O ratio variation within one sample of each group of GFM imaged with STEM

6. Conclusions

Particle sizes derived from methods in liquid (LD) appear to be significantly higher than from imaging and care needs to be applied to compare like with like, i.e. number based distributions and volume derived distributions for primary particles as well as agglomerates and aggregates. Energy transfer to the liquid sample during sonication can change the size distribution and this apparent PSD change is correlated not only to the shape of individual particles but also to their surface properties.

Different size fractions can be correlated with the help of imaging and spectroscopy techniques either to individual particles or agglomerates and aggregates. For the calculation of overall C/O ratios the morphology of individual particles as well as the amount and nature of impurities and or contamination needs to be considered.

7. Acknowledgment

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