Morphological analysis and Sample preparation of Particulate Graphene oxide materials

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1. Introduction

Graphene oxide shows immense potential due to its physico-chemical properties that can be further tailored to specific applications through functionalization[1]. The well-known Hummer method is a synthesis method that can be easily scaled up[2]. Applications such as catalysis, biomedicine, electronic devices, and water filtration enable GO as a promising material for the future[3]. The present study focuses on the morphological characterization of graphene oxide flakes. The complexity of these materials varies substantially. Within the European project ACCORDs a framework for the physico-chemical characterization of complex graphene-family materials (GFM) is developed, with the focus on methods capable of imaging and with final correlation to the biological behaviour of the analysed materials.

2. Materials

The materials investigated in this study are three types of GO flakes with different origins. The “ideal” case of GO flakes from Graphenea represents flakes which are well dispersed, non-overlapping when prepared on a substrate, and can, therefore, serve as a reference regarding size and shape analysis. More complex but well documented regarding synthesis conditions are samples that were synthesised by University of Turin (“UniTo”) within the ACCORDS project. These exhibit nanoscale characteristics such as porosity, edge roughness combined with significant degree of agglomeration/aggregation and the lateral size spans several orders of magnitude. The commercial samples from Haydale are provided as powders, dispersed in water, as inks as a mixture of resin and GO, with different functionalization and tend to agglomerate heavily.

3. Sample Preparation

Sample preparation must be tailored to the specific measurement employed and each material requires unique solutions regarding substrate, dilution, dispersion media and deposition technique to obtain separated flakes with minimal overlap.

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i) Graphenea samples were prepared as dispersion in Millipore water isopropanol mix on both holey carbon TEM grids and silicon wafer.
ii) UniTo samples were prepared in Millipore water similar to i).
iii) Raw powder samples from Haydale were deposited as is on self-adhesive carbon. The same powders were further embedded in polyacryl resin and then ground and polished to investigate the cross-sectional area. The powders were dispersed in water and drop-casted on silicon wafer. They were also provided as inks which were brushed on top of silicon wafer.

4. Characterization method

A SEM of type Supra40 (Zeiss) equipped with a secondary electrons (SE) InLens detector was utilized for this study. For samples deposited on TEM grid a dedicated sample holder for the scanning transmission electron microscopy in SEM (STEM-in-SEM) mode was used. With the InLens, the SEs emitted within a very narrow solid angle (SE1) are detected with the option to correlatively analyse the transmitted electrons, which are detected by the conventional SE Everhart-Thornley detector.

5. Image analysis

To accurately measure the lateral particle size, the electron microscopy (EM) data was processed using the software package ImageJ[4]. For the Graphenea material semi-automatic evaluation with a pre-processing median filtering, ISOData thresholding followed by a manual correction of faulty segmentation were performed. The images of the dispersed Haydale samples were automatically processed with the StarDist algorithm[5] to obtain the regions of interest of the flakes/particles, accounting for limited amount of overlap with only minimal manual post processing. Embedded powder samples were analysed semi-automatically. For the UniTo materials we developed a particle classification scheme. Further, the pore amount within the GO particles was evaluated through semi-automatic analysis by measuring the ratio of flake area to defect areas within the flake visible in the EM images.

6. Results

For the Graphenea material (shown in Fig. 1) the area equivalent circle diameter (ECD), the minimum Feret and the (maximum) Feret were extracted. The ECD amounts to 1.34 µm, the minimum Feret to 0.91 µm and Feret to 1.47 µm.

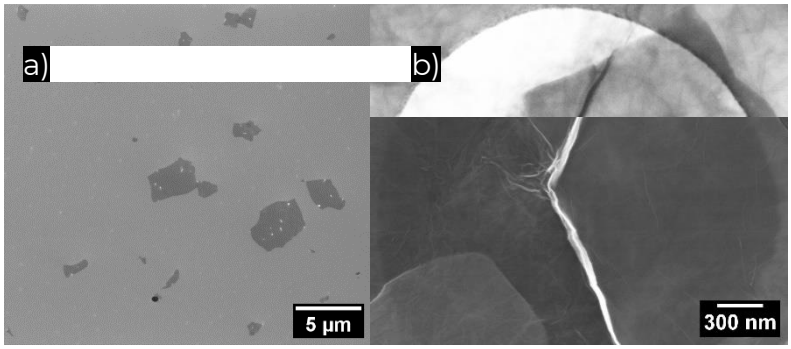

Figure 1: Graphenea sample as a) flakes on silicon wafer and as b) flake on holey carbon support (top: STEM in SEM; bottom InLens)

For the UniTo sample following dimensional properties have been determined: mean ECD ~1 µm, MinFeret ~0.47 µm, MaxFeret ~0.82 µm, with a pore area ratio of ~5% was obtained (with insufficient statistics as a proof-of-principle).

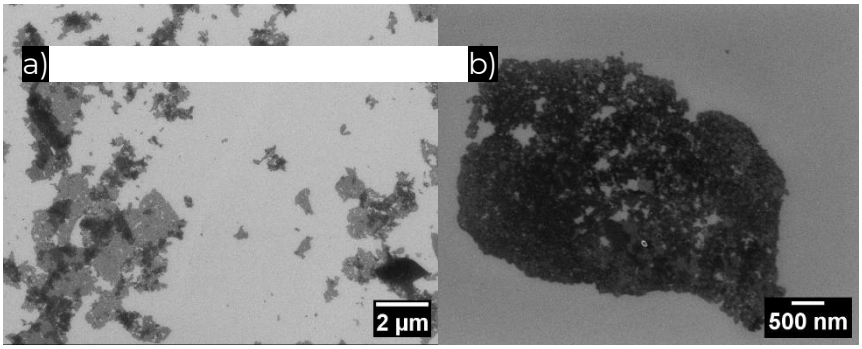

Figure 2: UniTo sample showing a) overlapping GO flakes and b) single flake with porous structure.

For the Haydale samples (Fig. 3) a distinction for the dispersed sample was made: the constituent particles were assessed separately from the agglomerated ones.

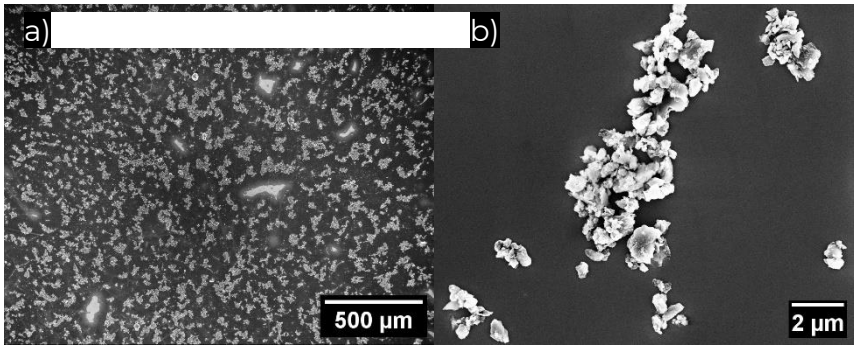

Figure 3: SEM of the Haydale sample powder dispersed in water a) at low magnifications showing agglomerations and b) at higher magnification showing constituent particles within an agglomerate.

Figure 4 shows the GO flakes embedded in resin (4 a) as part of the sample preparation process and within the inks as a mixture of resin and GO flakes.

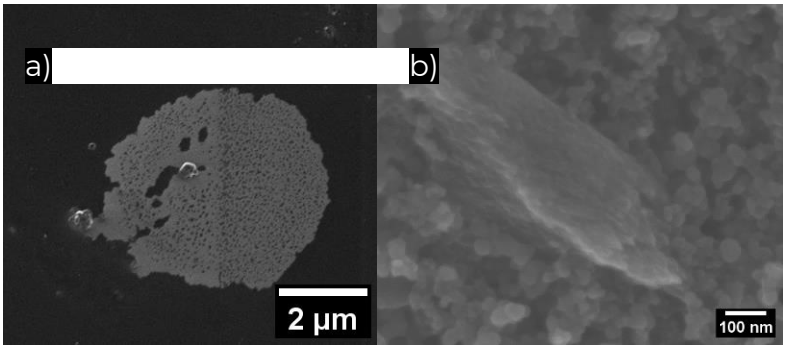

Figure 4: Haydale sample a) powder embedded in polyacryl resin b) GO flake as part of an ink.

7. Discussion

For each individual material each preparation method offers advantages and disadvantages or is not applicable. Drop casting works well for the Graphenea material allowing to accurately quantify the lateral particle size of the well-defined flakes. For the UniTo GO materials it is challenging to separate flakes from agglomerates and, therefore, only a qualitative assessment of the particle size distribution is currently possible. An additional feature, i.e., the pore amount/ area ratio, can be specified quantitatively within a certain error. For the Haydale samples agglomeration/aggregation of particles of the dispersed powders required to distinguish between the size of constituent particles and the size of agglomeration, leading to two different characteristic values per investigated sample.

The embedding preparation technique only works for powder samples but allows for the investigation of the particles in a similar environment to that of the inks (as the final nancomposite product).

8. Conclusion

It is imperative to find the suitable preparation method to enable the accurate and automatic analysis of the lateral size of GO flakes. Representativity of the analysis of EM images can be severely limited by non-optimal preparation, but also due to agglomeration/aggregation. These require both low and high magnification to capture the whole morphology picture. Existing automatic analysis algorithms are often too time-consuming, inflexible, and specific to completely assess the requirements of the shown complexity of GO materials.

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10. References

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