

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Effect of synthesis conditions, polymeric stabilizers and heat on graphene nanoplatelet dimensions and colloidal interactions	Experiment number: SC 5184
Beamline: ID02	Date of experiment: from: 27-08-2021 to: 30-08-2021	Date of report: 21-02-2022
Shifts: 9	Local contact(s): Dr. Lauren Matthews	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Laura van Hazendonk* ¹ , Marloes van der Horst* ¹ , Lisette Wijkhuijs* ¹ , Andrei Petukhov ^{1,2} , Remco Tuinier* ¹ , Mark Vis* ¹ , Heiner Friedrich ¹ ¹ Laboratory of Physical Chemistry, Chemical Engineering and Chemistry, Eindhoven University of Technology, Netherlands ² Van 't Hoff Laboratory, Dept of Physical & Colloidal Chemistry, Debye Institute, Utrecht University, Netherlands		

Report:

Aim

Graphene has the potential to revolutionize the field of printed electronics thanks to its high conductivity, chemical stability and natural abundance (1). We have previously developed conductive screen printing inks through the gelation of graphene-polymer dispersions (2). The gelation mechanism of these inks and the role of polymeric stabilizers therein is still poorly understood. Using small-angle X-ray scattering (SAXS), we aim at mapping the effects of synthesis parameters on the dimensions of graphene nanoplatelets (GNPs) at low concentrations, and the effects of polymeric stabilizers on the colloidal interactions and stability of GNPs at higher concentrations.

Methods

To study the effect of synthesis parameters on GNP dimensions, GNPs were prepared from raw graphite according to an intercalation and thermal expansion protocol followed by exfoliation via high-shear mixing as published previously (2, 3). The exfoliation conditions were varied to investigate the effect of several additives, additive concentrations and solvent choice on the platelet morphology. The raw graphite source and intermediate products of the intercalation and expansion process were also studied to understand the morphological changes induced by these transitions.

Commercial GNPs with a diameter of 5 μm were dispersed in several solvents (water, ethanol, ethyl acetate) with a high-shear mixer. Several additives (ethyl cellulose, sodium deoxycholate) were added in varying concentrations to study the effect of additives on the GNP colloidal interactions.

All samples were brought to ID02 in quartz capillaries for the efficient measurement of a high number of samples. In addition, a series of dispersions with several additive concentrations were sedimented *in situ* to quantify their colloidal stability. Furthermore, several dispersions were heated *in situ* to investigate temperature-induced morphological changes.

Preliminary results

We investigated the production process of GNP through intercalation and thermal expansion of raw graphite (3). The WAXS pattern of raw graphite (Figure 1a) contains a peak at $q = 18.5 \text{ nm}^{-1}$, corresponding to the graphene layer spacing of 0.34 nm (4). Interestingly, this peak broadens and flattens significantly upon intercalation of graphite with small molecules, producing intercalated graphite (IG). After thermal expansion and intercalation, the typical graphene layer spacing returns. In contrast, the SAXS patterns (Figure 1b) reveal no changes after intercalation with the slope remaining -3.4 , while thermally expanded graphite (TEG) has a slope of -2.3 . The absolute slope increases slightly to -2.8 after exfoliation. The decrease in fractal dimension from raw graphite to GNP thus confirms exfoliation of the particles. Next, we will fit form factors to the SAXS patterns to extract deeper morphological information from these patterns. In addition, we will investigate how exfoliation conditions, e.g. solvent type and additive concentration, affect the GNP form factors.

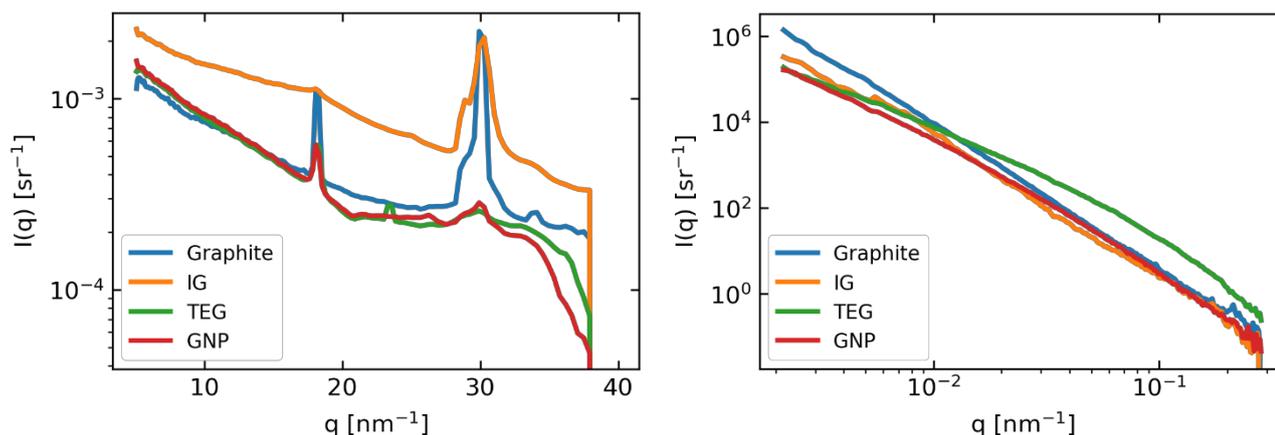


Figure 1 Evolution of SAXS (left) and WAXS (right) patterns for the processing of raw graphite into graphene nanoplatelets (GNP) via intercalation with small molecules to produce intercalated graphite (IG), followed by thermal expansion yielding thermally expanded graphite (TEG) and finally liquid-phase exfoliation resulting in GNPs. Slopes of the SAXS curves are -3.4 for raw graphite and IG, -2.3 for TEG and -2.8 for GNP.

To investigate the colloidal stability of GNP dispersions in ethanol with varying additive (ethyl cellulose) concentrations, we let our samples sediment inside the capillary overnight. After sedimentation, the scattered intensity at the top of the capillary increased with ethyl cellulose concentration, indicating a decrease in sedimentation rate (Figure 2). Therefore, it is concluded that additives can be used to tune the colloidal stability of GNP dispersions.

We produce graphene nanoplatelets via high-shear exfoliation of expanded graphite. This produces nanoplatelets with a range of thicknesses depending on the exfoliation conditions. To investigate the thickness distributions, we fitted a form factor for lamellar disks to the SAXS pattern. The procedure is illustrated in Figure 3 for two types of graphene nanoplatelets. The data shows that our in-house GNP is approximately ten times thinner and less polydisperse than its commercial counterpart. Next, we will investigate changes in the form factor (platelet stacking versus proper dispersion) and structure factor induced by the addition of additives. Although our GNP model system turned out slightly too large to characterize the full lateral dimensions of the particles, we expect to obtain significant insight by fitting form factors to the SAXS patterns according to the procedure detailed in Figure 3. We will complement the SAXS data with in-house dynamic light scattering measurements to obtain the full platelet dimensions. Next time, we would use a slightly smaller model system.

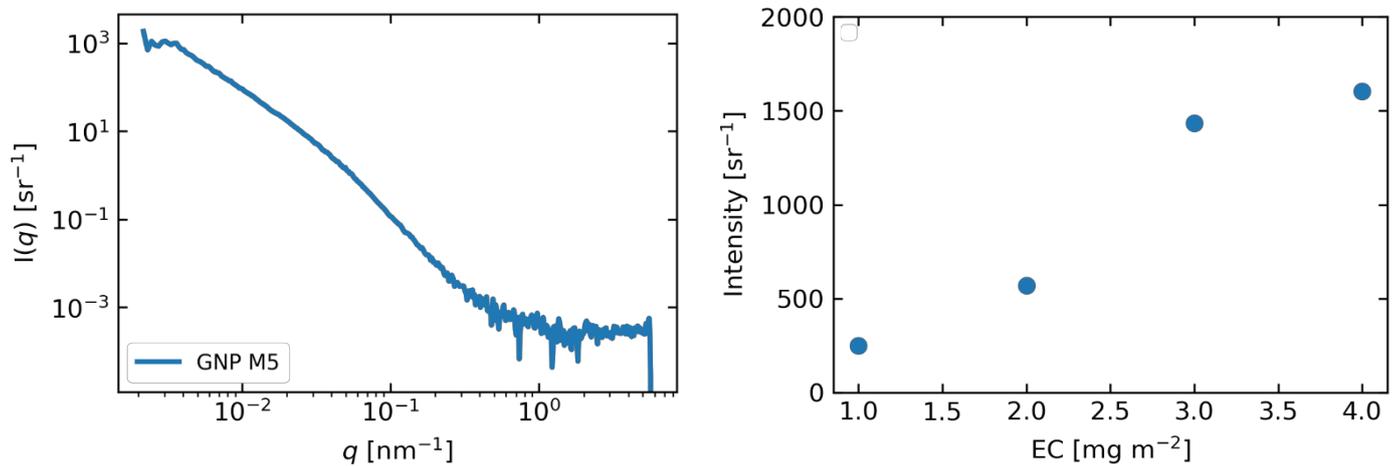


Figure 2 (left) Example SAXS pattern of a GNP dispersion. (right) Scattered intensity at the top position of capillaries sedimented overnight versus ethyl cellulose (EC) concentration. Intensity was measured at $q = 6.07 \cdot 10^{-3} \text{ nm}^{-1}$.

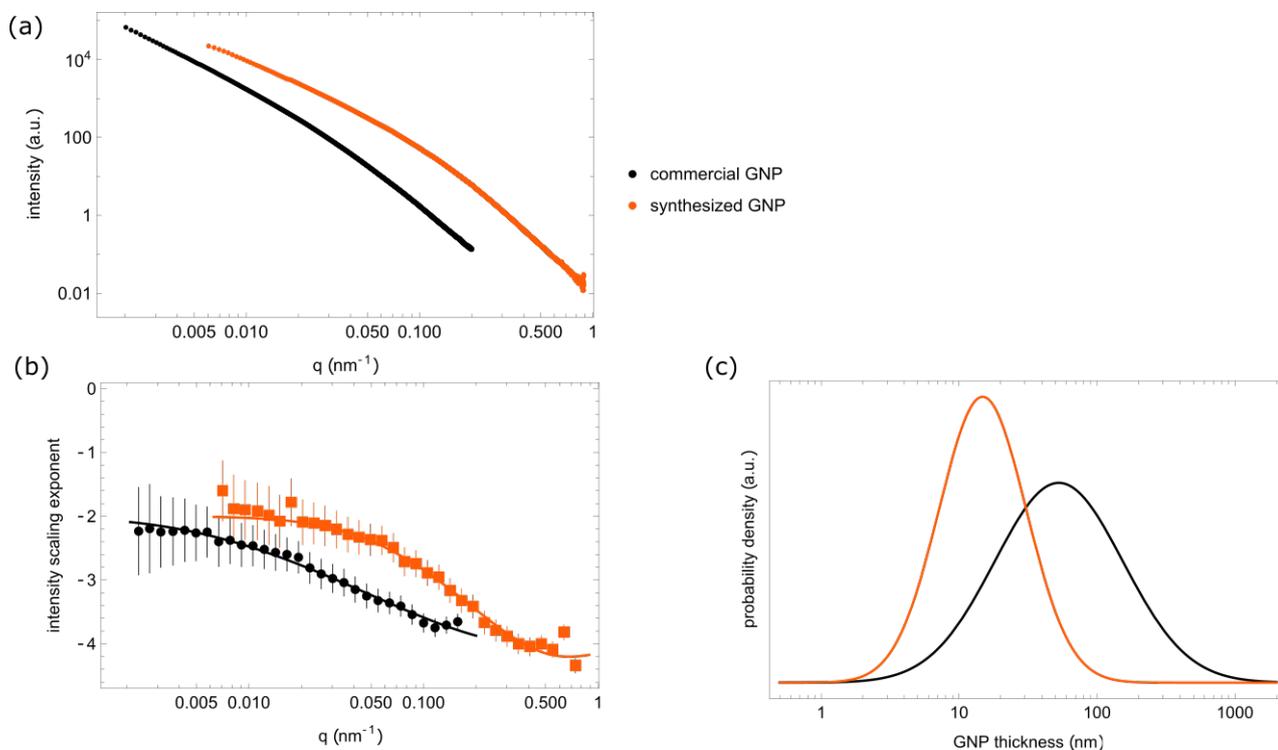


Figure 3 Derivation of platelet thickness distributions via fitting of the intensity power law decay for two types of graphene nanoplatelets (GNP): commercial GNP and in-house synthesized GNP. (a) Scattered intensities. (b) Slopes vs q extracted from the experimental data in panel a (points), as well as theoretical fits from the form factor based on polydisperse disks (curves). (c) Log-normal thickness distributions as resulting from the fits.

Further work

Full analysis of the dataset (>500 GB) is in progress. We are particularly interested in the effect of exfoliation conditions on GNP thickness, in the effect of stabilizers on interplatelet interactions expressed in the structure factor and the form factor (e.g. GNP thickness), in nematic structure formation during sedimentation and in changes in the platelet network during heat ramps.

Acknowledgements

We would like to thank Dr. Lauren Matthews for her support during the measurements at ID02 and also during the preparation and analysis stages. She will be added to the author list of a potential publication of this work.

References

1. G. Hu *et al.*, *Chemical Society Reviews*. **47**, 3265–3300 (2018).
2. K. Arapov *et al.*, *Advanced Functional Materials*. **26**, 586–593 (2016).
3. K. Arapov, A. Goryachev, G. de With, H. Friedrich, *Synthetic Metals*. **201**, 67–75 (2015).
4. H. Li *et al.*, *J Nanopart Res*. **15**, 1670 (2013).