EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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://wwws.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 form 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.

ESRF	**Experiment title:** Resolving In Situ Assembly of Nanocrystal Superlattices by Real-Time SAXS/WAXS	**Experiment number**: SC-4984
Beamline: ID02	**Date of experiment**: from: 10 September 2021 to: 13 September 2021	**Date of report**: 6 December 2021
Shifts: 9	**Local contact(s)**: BOESECKE Peter	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report: Colloidal PbS nanocrystals (NCs) exhibit low size/shape dispersity and size-dependent optical properties in the near-infrared range. The ability of PbS NCs to form highly ordered superlattices, e.g. upon solvent evaporation, makes them interesting for potential electronic and optoelectornic applications, such as solar cells, field-effect transistors, light-emitting diodes, photodetectors etc. Synchrotron *in situ* small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) are the techniques of choice for studying of the time-resolved assembly of NCs into superlattices with subsecond temporal and micrometer spatial resolution.

During the provided beamtime, we investigated the detailed transitions from the colloidal suspenstion to the self-assembled superlattice upon controlled solvent evaporation in real time using a combination of SAXS and WAXS. A dedicated sample environment [1] was used to obtain the targeted and controlled assembly conditions, where the NCs self-organized into ordered NC solids along the X-ray transparent silicon nitride membranes. Due to very low solvent evaporation rate (approximately 0.25 µl/min for heptane) the slightest changes in the superlattice states could be monitored.

The experimental parameters of the beamline were as follows. The energy of the incident X-ray beam was set at 12.46 keV and the beam size was 70 µm (vertical) x 120 µm (horizontal). The SAXS data were recorded by the Eiger2 4M detector at the sample-to-detector distance of 1.7 m. Images were collected with exposure times of 0.05 seconds. For the chosen exposure times no beam damage of the sample was observed.

Monodisperse PbS NCs were produced in our laboratory by a wet chemical method at different sizes in the range of 4-7 nm in diameter and stabilized by oleic acid ligands. After the synthesis, the nanoparticles were purified and different experimental protocols were used to obtain NCs

with various ligand grafting densities. Due to the facetted nature of the PbS core with {111} and {100} facets and different binding energies of oleic acids molecules to the {111} and {100} facets, the post-synthesis processing plays an important role in the obtaining of the higher or lower coverage of organic ligands on the inorganic NC core. Besides the influence of the NC size on the self-assembly outcome, the effect of the ligand grafting density on the superlattice transitions was studied in the allocated beamtime.

Figure 1 shows the time-resolved SAXS data revealing a transitions from the colloidal suspension into the NC superlattices – visible by the appearance of Bragg reflections – upon controlled evaporation in a solvent vapor saturated atmosphere. When the superlattice is formed, several transitions are evident, which are the subject of the ongoing analysis. In our previous publications, different superlattice structures during the self-assembly of PbS NCs have been observed, such as a hexagonal close-packed (hcp), body-centered cubic (bcc), body-centered tetragonal (bct), and face-centered cubic (fcc) [2-4]. Here, we aim to distinguish the role of the NC size and the ligand coverage on the assembly pathway and the final superlattice structure. The results are planned to be further analyzed and published in the near future.

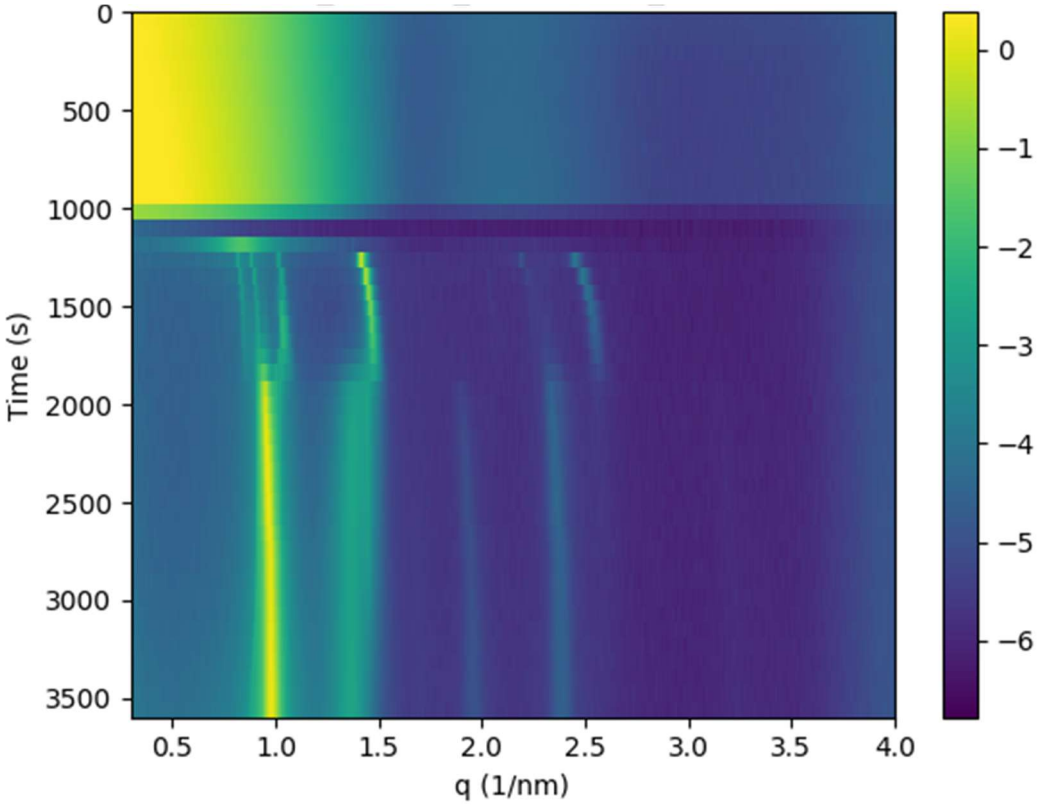

Figure 1. Time-resolved SAXS data during the *in situ* self-assembly of colloidal PbS NCs into superlattices upon controlled solvent evaporation.

[1] I. Lokteva, M. Koof, M. Walther, G. Grübel, F. Lehmkühler, Rev. Sci. Instrum. 90, 036103 (2019)

[2] I. Lokteva, M. Koof, M. Walther, G. Grübel, F. Lehmkühler, Small 15, 1900438 (2019)

[3] I. Lokteva, M. Koof, M. Walther, G. Grübel, F. Lehmkühler, J. Phys. Chem. Lett. 10, 6331–6338 (2019)

[4] I. Lokteva, M. Dartsch, F. Dallari, F. Westermeier, M. Walther, G. Grübel, F. Lehmkühler, Chem. Mater. 33, 6553 (2021)