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Experiment Report Form

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Once completed, the report should be submitted electronically to the User Office via the User Portal:

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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

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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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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:** Formation of supraparticles of semiconductor nanocrystals	**Experiment number**: SC-4487
Beamline: ID02	**Date of experiment**: from: 10-03-2017 to: 13-03-2017	**Date of report**: 08-09-2017
Shifts: 9	**Local contact(s)**: Rajeev Dattani	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

We have performed small-and-wide angle X-ray scattering (SAXS and WAXS) to study the self-assembly of iron cobalt oxide (FeCoO) nanocrystals (NCs) in three dimensional crystalline supraparticles (SPs) through spherical confinement. [1,2] So far the formation of SPs has been investigated only through theoretical simulations from analysis of the final product, but in this experiment we have observed for the first time the formation of the SPs *in-situ* through X-ray scattering.

Spherical SPs have been introduced recently [1] and they are formed through the self-assembly of NCs in the spherical confinement of an oil-in-water emulsion. The NCs are firstly dispersed in an oil phase (cyclohexane) in contact with a water phase containing: surfactants, to stabilize the two phases, and sugar, to increase the viscosity of the system. The two phase system is then emulsified through the application of a shear force using a homebuilt shear cell, resulting in an emulsion of oil droplets containing NCs in the water phase. The resulting emulsion is then put at 68°C in order to evaporate the oil phase. While shrinking due to evaporation, the oil droplets will pull the NCs together until final crystalization into SPs.

For our experiment we brought the shear cell, the oil phase and the water phase from Utrecht and we performed the emulsification at ESRF. The emulsion was then put in a vial laying on an heating plate at 68°C and folded by heating foils. The temperature was monitored with a thermocouple and kept constant at 68±2°C. The emulsion was then pumped through a capillary, with the use of a peristaltic pump, where the droplets were probed with X-rays (Fig.1). The droplets were continuously heated and pumped through the capillary for 6-7 hours until crystalization occurred.

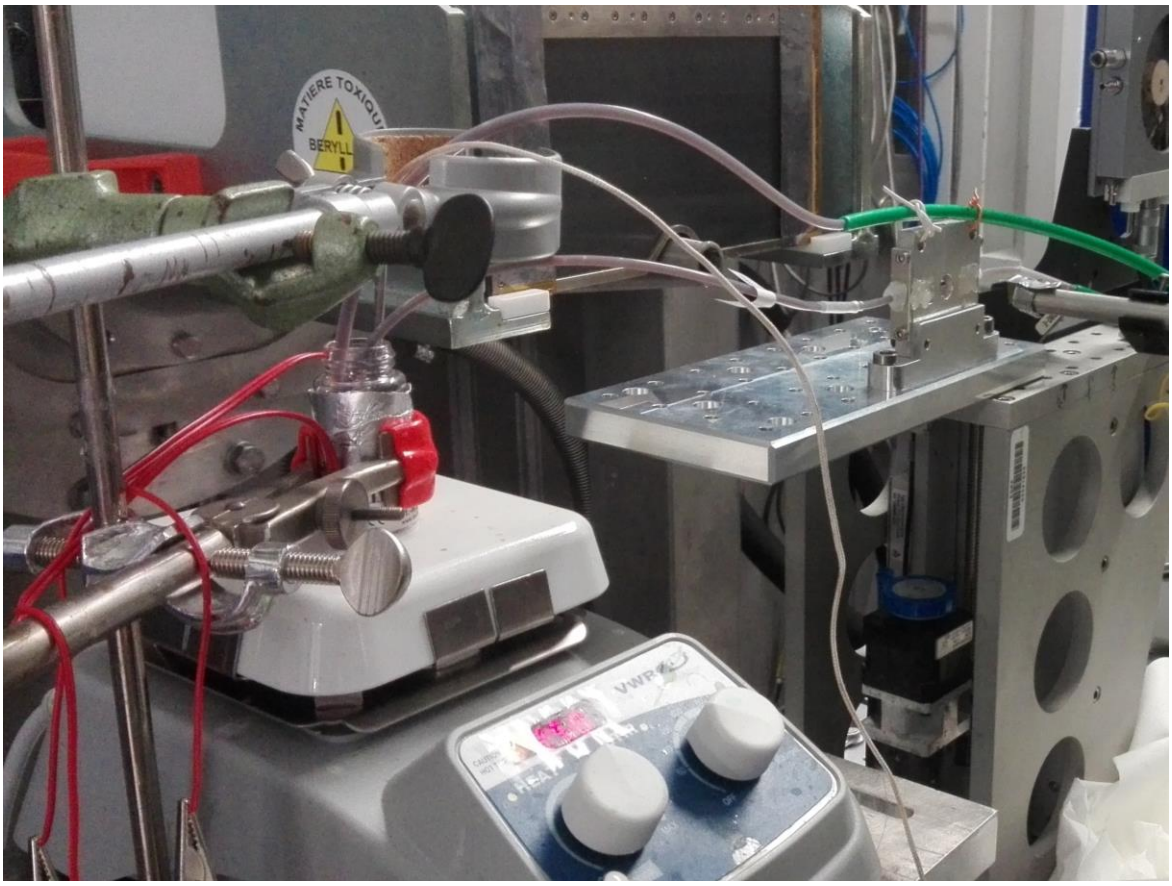

Figure 1: Digital picture of the setup used for the measurement

The SAXS measurements have been performed with three different detector distances (1-5-20 m), in order to explore the full q range, probing the sample for 30 ms and averaging the signal over ten measurements. In particular, with the detector set at 1 m we probed the q values related to the single NCs (size ~ 10 nm), while with the detector at 5 and 20 m we probed the q range corresponding to the oil droplets in water (size ~ few μm). In the measurements the form factor of the NCs is clearly visible, and the depth of the peaks indicates a relatively good monodispersity, around 7%, also confirmed by *ex-situ* TEM. The form factor of the droplets is also visible in the late stages of the experiments, but the very small depth of the peaks indicates a quite large polydispersity (around 20%), as previosuly observed in perliminary experiments in Utrecht (Fig.2).

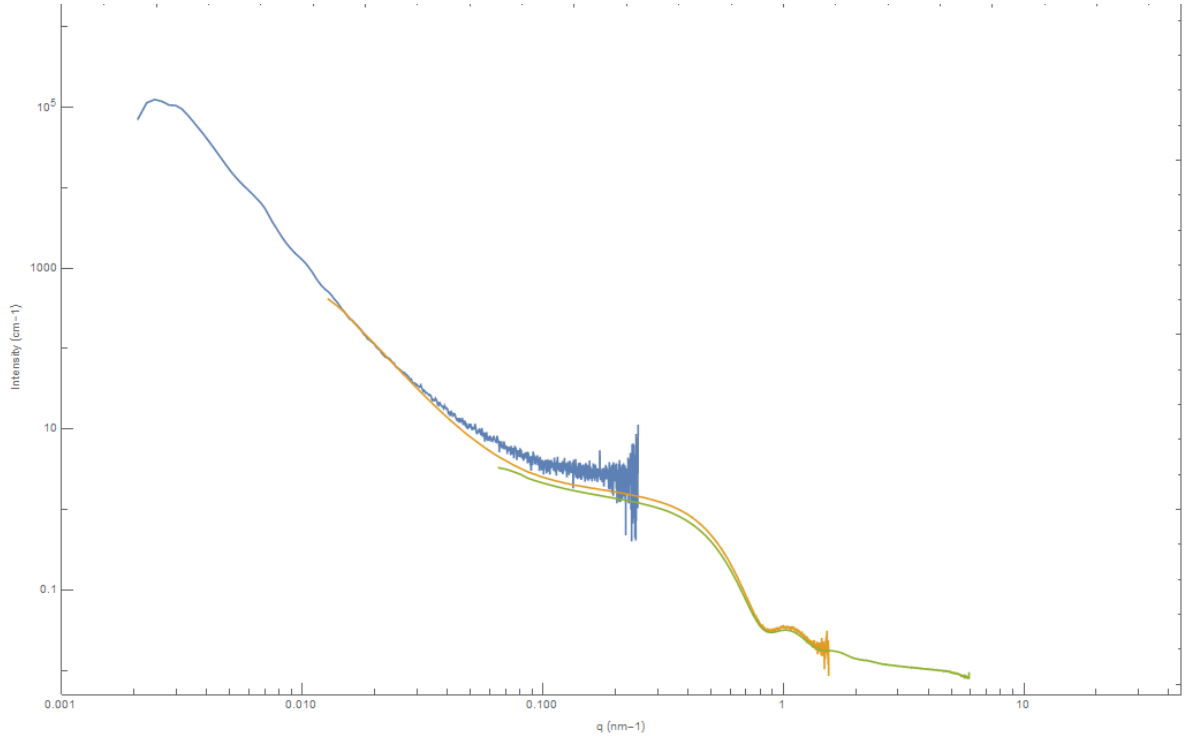

Figure 2: SAXS data of the probed emulsion at three different detector distances: 1 m (green), 5 m (yellow) and 30 m (blue).

During the experiment, we observe a clear increase of the volume fraction of the NCs in the droplets , which leads to the crystalization of the NCs into an FCC lattice. The crystallization kinetics are clearly visible from the appearance of structure factor peaks in the scattering data, which also show that the NC lattice contracts over time. Preliminary analysis of the data allowed us to index the structure-factor peaks up to 18 FCC reflections, which highlights the degree of long-range order of NCs inside the SP FCC lattice (Fig.3).

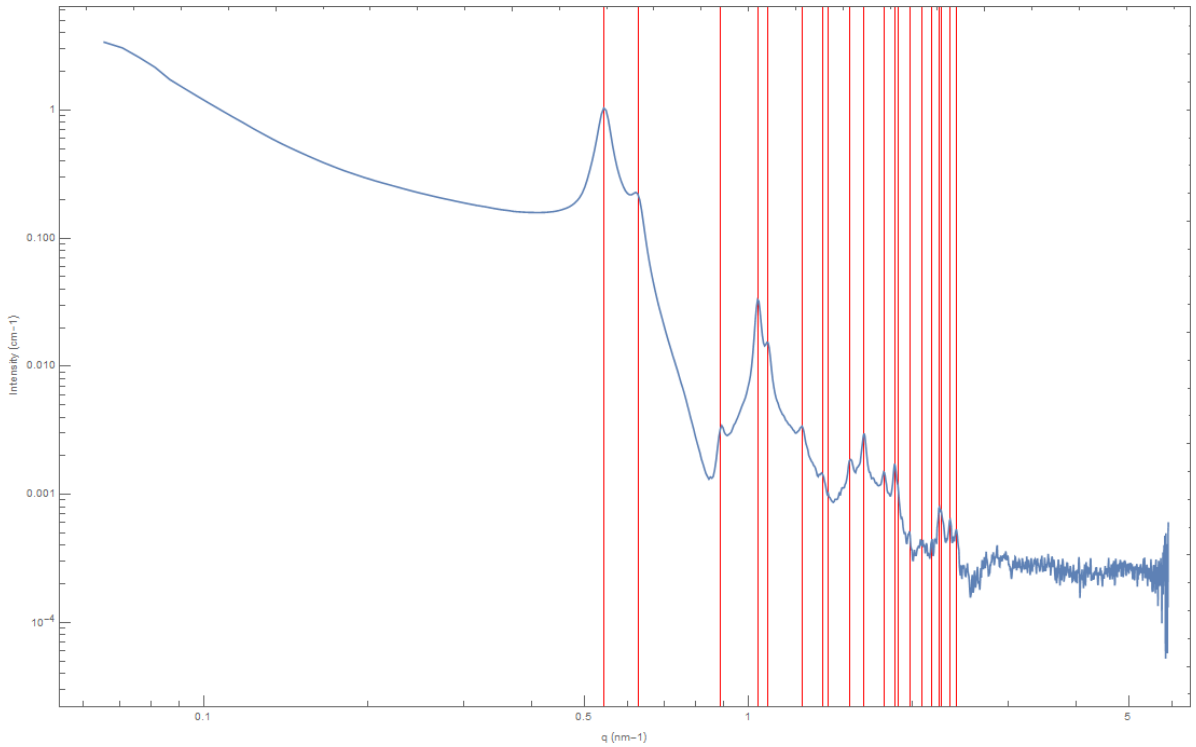

Figure 3: SAXS data of the crystalized sample (blue) with indication of calculated FCC reflections (red)

Concerning the WAXS data, we managed to follow the evaporation of the cyclohexane through the decrease in the scattering signal associated to it, thus corroborating the results observed with SAXS measurements.

For each experiments we performed static measurements over samples of SPs and NCs already characterized in Utrecht through TEM, in order to have references, and we also performed measurements of different background solutions for a better analysis of the data. All the samples were collected at the end of the experiment and analyzed through *ex-situ* TEM and STEM in Utrecht, where we confirmed the formation of the SPs with FCC crystal structure (Fig. 4).

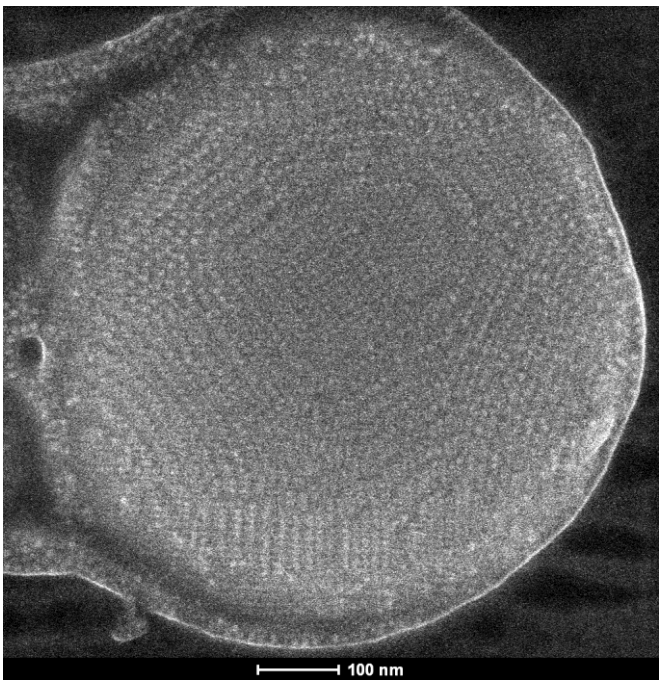

Figure 4: SE-STEM image of one of the SPs synthesized during the experiment; FCC crystal facets are clealry visible on the top and on the sides.

To summarize, we observed for the first time the *in-situ* formation of SPs from the self-assembly of NCs in the spherical confinement of an oil-in-water emulsion through X-ray scattering. In particular we performed SAXS measurements at three different detector distances in order to be able to follow the evaporation in the full q range. From scattering data we clearly observe the form factor of the NCs as well as of the oil droplets, from which we can extract the size, polidispersity and volume fraction over time. The latter is particularly interesting for us as it allows us to see the evolution of the spherical confinement over time, from the just-formed droplets to the final crystalization in SPs. The scattering data clearly show the crystalization of the NCs in SPs characterized by an FCC structure. After background subtraction, we preliminarly managed to index up to 18 reflection of the FCC crystal. We are currently working on fitting the complete scattering curve for all recorded frames in time, to obtain a full time-resolved picture on this exciting crystallization process.

[1] B. de Nijs, A. van Blaaderen *et al.*, Nat. Mater. **14**, 56-60, (2015)
[2] F.Montanarella *et al.*, ACS Nano ASAP (2017) DOI:10.1021/acsnano.7b03975