EUROPEAN SYNCHROTRON RADIATION FACILITY

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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

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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:** Oriented attachment of PbSe nanocrystals into atomically coherent honeycomb supercrystals	**Experiment number**: SC-3786
Beamline: ID-10	**Date of experiment**: from: 06-02-2014 to: 10-02-2014	**Date of report**: 29-7-2014
Shifts: 12	**Local contact(s)**: Federico Zontone and Oleg Konovalov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

We performed GI-SAXS/WAXS measurements on the oriented attachment of colloidal PbSe nanocrystals (~5nm diameter) into atomically coherent supercrystals at the toluene-air interface [1,2]. For the experiments we used a large area teflon cell in which 28 mL of immiscible liquid ethylene glycol (EG) was loaded. We also added various amounts of oleic acid to EG. On top of this substrate we deposited 1 mL of the nanocrystals in toluene. Self-organization and oriented attachment was induced by evaporation of the toluene at room temperature; the ligands which stabilize the quantum dots in solution are gently stripped of and are dissolved in the EG substrate. This exposes the reactive nanocrystal facets which allows for bond formation between the nanocrystals. Complete evaporation of the toluene took approximately 60 minutes per sample. The toluene-air interface drops upon toluene evaporation. To keep the setup well-aligned with the X-ray beam at grazing incidence we adjusted the height of the setup with a moveable stage, which could be controlled from the hutch. With this method we were able to follow the nancrystal oriented attachment at the toluene-air interface until complete evaporation of the toluene solvent.

The goal of our experiment was to follow the attachment process in-situ. We proposed a model that consists out of (i) self assembly of the quantum dots in a 2D monolayer, (ii) stripping of the nanocrystals from their ligands, (iii) decrease of the nanocrystal-nanocrystal distance followed by attachment into a supercrystal. The most fascinating structure is the honeycomb supercrystal, which has its' constituent particles in two different planes of height. We are currently still trying to explain this peculiar phenomenom.

During this experiment we used a bright and narrow beam of X-rays with a photon energy of 20.7 keV to probe the liquid air surface. The SAXS pattern was recorded simultaneously with the WAXS signal, which allowed us to follow not only dynamics on the nanoparticle scale, but also follow the atomic alignment of particles. We have been able to follow these dynamics for a supercrystal with square geometry; we observed particle ordening, shrinking of the superstructure (by removal of ligands) while atomic order started to appear and was preserved throughout the shinking process. We are currently working on more elaborate data-analysis, such as following the peak-width over time and analysis the WAXS data in more detail.

To illustrate the obtained results so far, in figure 1a-d we show the evolution of the SAXS pattern over time. The whole experiment was done over a timespan of 2 hours which equals 356 frames. The data obtained was quite noisy; the particles sustained beamdamage and we observed visually the presence of floating patches, which resulted in a 'flickering' of the signal. After approximately 5 minutes we observe two bragg rods in figure 1b, at $q_y = 0.93$ nm^{-1} which proves that we have an in-plane structure with a periodicity of a = 6.8 nm. We attribute this to a monolayer of particles which are separated by interdigitated oleic acid ligands. Over time more peaks appear, as can be seen in figure 1b-d, which can be ascribed to a combination of an hexagonal ordening combined with a square ordening of particles;

The ratio of $q_1 : q_2 : q_3 = 1 : \frac{2}{\sqrt{3}} : 2$ is consistent with a mixture of patches with two different geometries, namely square and HCP, which are both indicated in figure 1g.

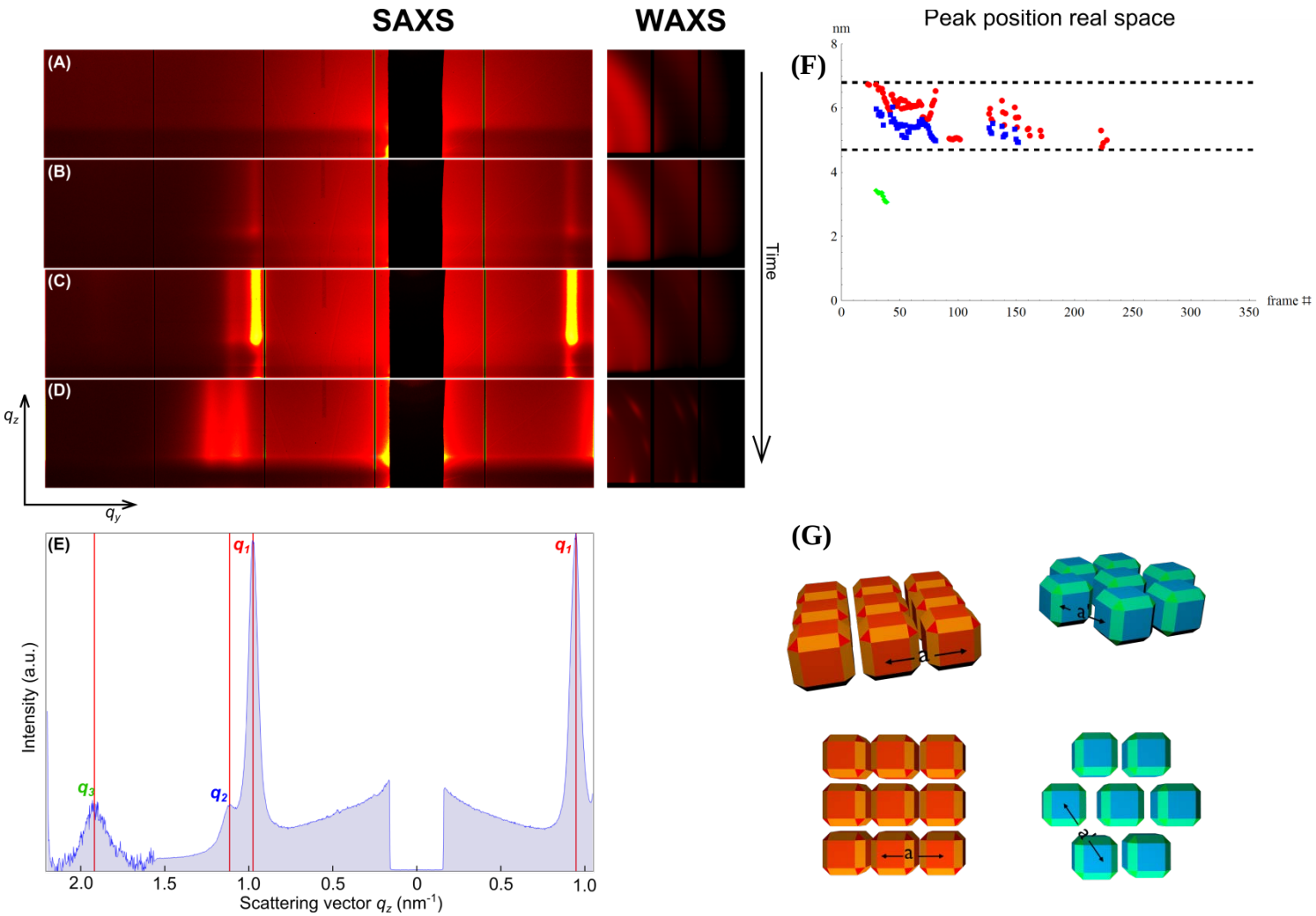

Figure 1: (A-D) evolution of SAXS and WAXS patterns over time. (E) integrated intensity of one of the SAXS patterns, indicating the peak positions and names by color. The data >1.6 nm^{-1} was multiplied by 20 for clarity. (G) side and topview of the obtained structures.

Figure 1e shows one of the SAXS patterns which is integrated over 10 q_z pixels above the horizon. By fitting all the peaks with guassians, the relative position, intensity and FWHM can be determined. Figure 1f shows the results of the peak position followed over time. The data is noisy, due to beam damage and the presence of floating patches. The interparticle distance decreases over time by a lengthscale that corresponds to interdigitated oleic acid ligands. Moreover, as can be seen from the WAXS data, atomic order is preserved throughout this shrinking process.

We conclude that the nanocrystal attachment occurs via a self-organization process; the particles order themselves on the liquid-air surface, align themselves atomically and approach while the ligands get stripped of and nanocrystal-nanocrystal bonds are formed. We have combined this data with ex-situ and in-situ TEM studies of the formation of the square supercrystals. New insights can be obtained from the results of the

presented experiment, which are currently being analyzed in more detail. A publication based on these data is targeted.
We would like to gratefully acknowledge dr. Oleg Konovalov and dr. Federico Zontone for their support during these experiments.

[1] M.P. Boneschanscher et. al., *Science* **2014**, 344 (6190), pp. 1377-1380
[2] W.H. Evers et. al., *Nano Lett.* **2013**, *13* (6), pp 2317–2323