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- 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 supercrystals with honeycomb nanogeometry	**Experiment number**: SC-4125
Beamline: ID-10	**Date of experiment**: from: 11-03-2015 to: 17-03-2015	**Date of report**: 04-05-2015
Shifts: 12	**Local contact(s)**: Giovanni Li Destri / Oleg Konovalov	*Received at ESRF:*

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Report:

We have performed grazing-incidence small-and-wide-angle X-ray scattering GIS&WAXS to study the reactive self-assembly of PbSe nanocrystals into atomically coherent superlattices at the liquid-air interface[1,2]. Previous experiments have been focussed on the formation of superlattices with a square nanogeometry, a publication of this work is in preparation. These new experiments have been focussed at studying the formation of the nanocrystals with a honeycomb nanogeometry.

During ex-situ experiments in our lab in Utrecht the formation of the honeycomb superlattices has been found to be extremely air-sensitive. In order to have a cleaner atmosphere during our experiments at ID10, we designed and build a new sample cell to create water-and-oxygen-free environment, see figure 1A. The new setup allows for repeted flushing of the cell with argon, followed by evacuating the present gasses with a vacuum pump. By repeating this process >4 times, still leaving a gentle argon flow over the cell, we ensure that our atmosphere is as clean as possible. Moreover we lead the argon stream through a bubbler with toluene, which creates a sliht vaporpressure of toluene in the sample cell, mimicking the conditions in the glovebox, hence the conditions in which we grow the superlattices *ex-situ* as close as possible.

For the experiments we used a large-area teflon cell in which 28 mL of ethylene glycol (EG) was loaded as a liquid substrate plus an additional amount of ligands, varied between experiments. On top of this substrate we deposit 0.5 – 1 mL of nanocrystal dispersion in toluene. The self-assembly and oriented attachment is induced by evaporation of the toluene at room temperature and subsequent gentle stripping of the nanocrystal capping ligands by the EG. During this process the reactive {100} facets are exposed and allows for bond formation between the nanocrystals, either in superlattices with a square nanogeometry, or in supecrystals with a honeycomb nanogeometry depending on the experimental conditions. The honeycomb crystal is most fascinating, since it has it's constituent nanocrystals in two planes of different height.

We chose perform the experiments at an X-ray energy of 10keV for numerous reasons. Firstly we observed during previous experiments (SC-3786 and HC-890) that PbSe is very sensitive to X-rays. At 10keV we are under Pb and Se absorption edges (both ~13keV), which should result a significant reduction of absorption of the X-rays. Moreover, there were several geometric constraints which had to be fulfilled, which were found to be optimal at 10keV:

- The WAXS detector should not block the line of sight of the SAXS signal. To increase the angles of the atomic reflections w.r.t. the SAXS line of sight, we can go to lower X-ray energies.
- The {200} and {220} reflections should be visible on the WAXS detector.

Some results from initial data analyses on succesful experiments are summarized in figure 1B-D. Figure 1B shows the GISAXS pattern of the honeycomb superlattice. There are up to four structure factor rods visible, with relative positions $1:\sqrt{3}:2:\sqrt{7}$, indicating a high degree of order within the obtained superlattice. As

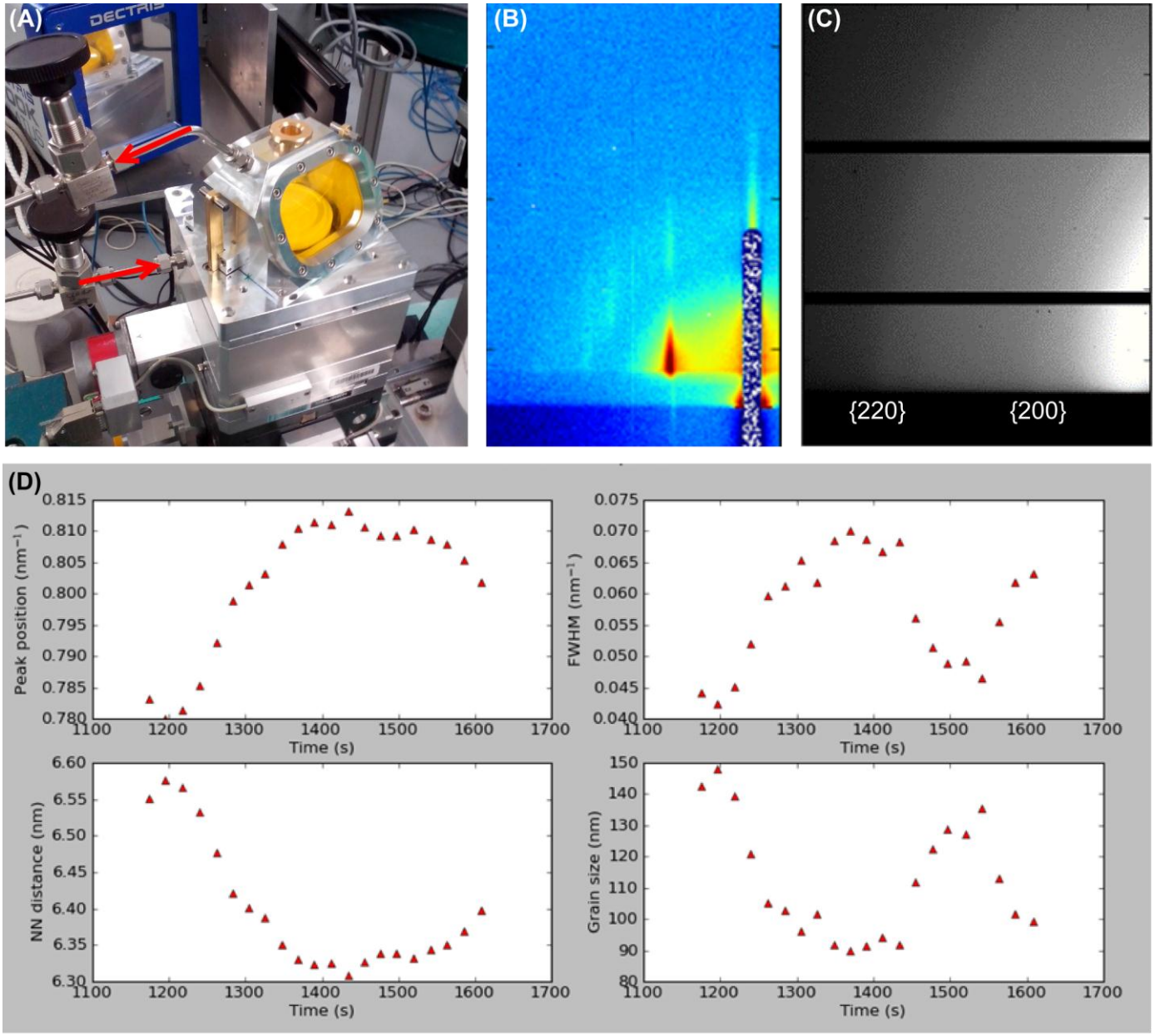

Figure 1: (A) The experimental setup designed and used for these experiments. The red arrows indicate where the argon gas is inserted and the vacuum pump is connected to the cell. (B) GISAXS pattern of the honeycomb superlattice. (C) WAXS pattern corresponding to (B). The diffraction from PbSe is slightly visible, noise reduction through background subtraction is currently investigated. (D) Results from the initial data analyses. The top left and right panels show the position and width of the first peak respectively. The bottom left and right panels are the nanocrystal-nanocrystal separations within the superlattice and domain size of the supercrystals respectively.

soon as the small-angle scattered signal appear, also atomic reflections were faintly visible, as seen in figure 1C. The bright rim in the bottom right area above the horizon was cross checked to be an ethylene glycol reflection. From the position of the two faint rings we deduced them to be reflections from the {200} and {220} atomic planes. Moreover the {200} ring has an decreased intensity above te horizon and an increased intensity at a higher angle, which is a first indication that the particles also have their {111} axis perpendicular to the liquid substrate. Moreover the reflections appear to have a smaller width than the same particles in solution in a capillary, which in turn indicates that the crystalline domain size has grown. This still has to be verified by fitting the data, but this is still ongoing.

We have been able to follow the dynamics of this particular type of reactive self-assembly over time. Each frame was integrated over ten seconds. We determined the position of the first diffraction rod over time. After approximately 1200 seconds (20 minutes) the first diffraction rod was visible, which starts to migrate to higher q-values over the course of 200 seconds. After 1400 seconds the position remains rather constant, only to decrease slightly. This indicates that the particles approach eachother, to a certain distance, after which they slightly move apart again. When we assume the particles to be octahedrally connected, which was confirmed in during previous studies [1], one can calculate the nearest neighbour (NN) distance from the position of the first diffraction rod $\mathbf{q_1}$ rather simple, $NNdistance = \frac{4\pi}{\sqrt{6}*\mathbf{q1}}$, and quantify the motion of the particles. The initial NN distance of 6.55 nm is slightly larger than the original particle size (6.0 nm), which can be explained by the presence of interdigitated capping ligands between the particles. When these are gently stripped off, the particles approach eachother with their exposed {100} facets and start to form atomic bonds. As also reported by Boneschanscher et al. [1] there appears to be the formation of necks in between the particles in the octahedral honeycomb lattice, which is seen by an increase of NN distance w.r.t. the initial particle size. We observe a slight necking, in the order of roughly 7% of the intial particle size, in between the particles in the superlattice. Since we vary the sample position between each frame slightly, the peak width fluctuates, as we are presumably measuring different domains each time.

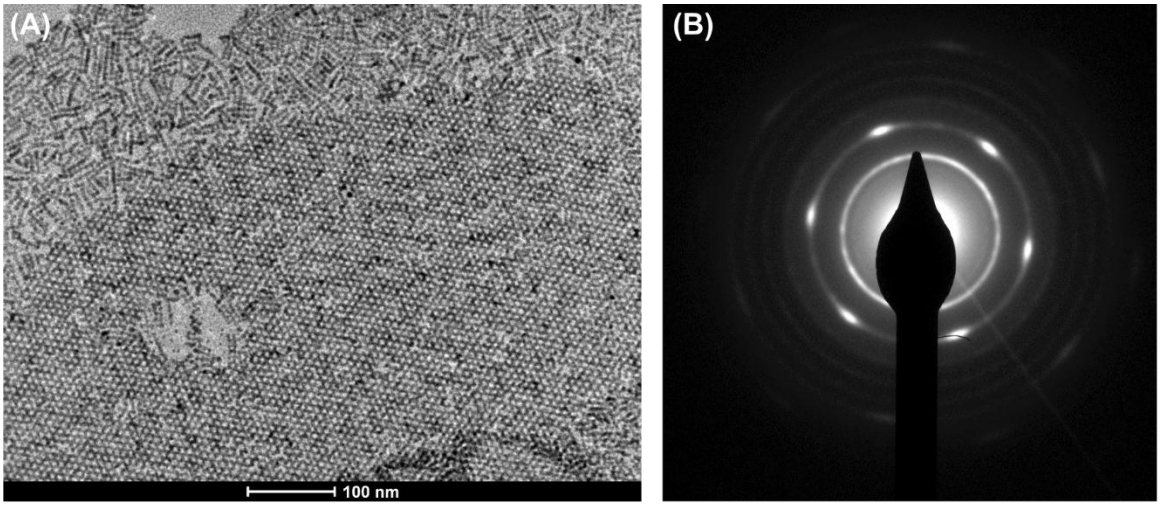

Figure 2: (A): TEM image from a sample scooped from the same experiment as in figure 1. Honeycomb superlattices are seen in large quantities, with linear structures in fewer numbers as defects attached the honeycombs. (B) Diffraction pattern corresponding to area in (A), showing that the nanocrystals have their <111> direction perpendicular to the surface and that they have their atomic planes aligned with respect to eachother.

The validity of the conclusions drawn from the X-ray scattering experiments is enhanced by the fact that we were able to look at the measured structures *ex-situ*, something previously impossible for these and other semiconductor structures[2]. After doing the scattering experiments, we scooped several samples of the liquid substrate on transmission electron microscopy (TEM) grids for further analysis. The structures

obtained during these experiments are shown in figure 2A-B. Figure 2A shows a large area overview of a honeycomb nanocrystal superlattice. Some linear structures are seen near the edges of the honeycomb structure and are well known defects, as seen in previous studies [1,3]. Electron diffraction confirms that the particles have their atomic planes aligned w.r.t. eachother and have their <111> direction perpendicular to the substrate. These results corroborate the results seen in the X-ray scattering experiments.

The results presented only show data from one of many experiments performed. To summarize we have designed and build a new setup to study air-sensitive reactive nanocrystal self-assembly *in-situ*. This allowed us to back up our conclusions drawn from the X-ray scattering experiments with electron microscopy and electron diffraction. We measured the dynamics of reactive self-assembly of PbSe nanocrystals into honeycomb superlattices with both GISAXS and WAXS. It is shown that the initial formed lattice contracts, where the particles get stripped of their ligands and approach eachother to form atomic bonds. The actual bond formation between particles, leading to an increased crystalline domain and hence thinner WAXS peaks w.r.t. individual particles, has not been measured before. As stated before, we are currently still doing more data analyses on different performed experiments and investigating methods to extract more information from the WAXS signal. We hope to combine these measurements with additional *ex-situ* TEM experiments and monte-carlo simulations. A publication based on this data is targeted.

We would like to gratefully acknowledge dr. Giovanni Li Destri and Oleg Konovalov for their support during the experiments.

[1] M.P. Boneschanscher et al., *Science* **2014**, 344 (6190), pp. 1377-1380

[2] F. Pietra et al., *Nano Lett.* **2013**, 12 (11), pp. 5515–5523

[3] W.H. Evers et al., *Nano Lett.* **2013**, 13(6), pp. 2317-2323