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ESRF

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:** Monitoring Oriented Attachment in PbS Nanocrystal Honeycomb Superlattices	**Experiment number**: SC-4033
Beamline: ID03	**Date of experiment**: from: 06/05 2015 to: 09/05 2015	**Date of report**: 02.03.2016
Shifts: 9	**Local contact(s)**: Maciej Jankowski	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Marcus Scheele, University of Tuebingen*

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Report:

The aim of this experiment was to investigate the role of oriented attachment during the self-assembly of PbS nanocrystals into ordered superlattices. We have recorded large sets of diffraction patterns with 2-dimensional grazing incidence small angle x-ray scattering (GISAXS), grazing incidence x-ray diffraction (GIXD) and x-ray reflectivity (XRR) measurements.

Experimental description:

The PbS nanocrystal samples were synthesized by a previously reported method.[ACS Nano 2014, 8 (6), 6363–6371] The nanocrystals were precipitated by the addition of anhydrous ethanol, the suspension was centrifuged for 5 min at 4500 rpm, the supernatant discarded and the precipitate dissolved in anhydrous hexanes. It was washed two more times on adding anhydrous ethanol and one more time with acetone. Self-assembly was achieved by slow evaporation of the solvent from the nanocrystal suspension placed on a plane Si wafer of 1 cm x 1 cm as substrate at room temperature. In a typical preparation, 500 µl of PbS nanocrystal hexane dispersion (0.5 mg/mL) were mixed with 50 µL of toluene in a vial. The vial was loosely capped with a wet lid with hexane and the solvent allowed to evaporate at room temperature for at least 16 h.
For GISAXS, the X-ray beam impinged under a grazing angle of 0.2° on the sample surface and the scattering pattern was detected using a 2D Pilatus 300K detector at a distance of 170 cm from the sample. The energy of X-rays was 12.9 keV. GIXD and XRR scans were recorded at the same energy using a MaxiPix detector. For GIXD, an incidence angle of 0.1 deg -i.e. well above the critical angle of total external reflection – was used. The respective resolutions taking into account the beam size and the pixel to pixel distance were 0.05 deg corresponding to 0.0055 $Å^{-1}$ for the laterally slitted down Maxipix detector ("GIXD regime") - i.e. the in-plane resolution of the line scans in the GIXD regime made via moving the delta arm (i.e. detector horizontal angle arm). For XRR, the data was recorded in specular geometry and corrected for the background as well as the beam footprint.

Main results:

The results of this beamtime have – in part – already been published here:

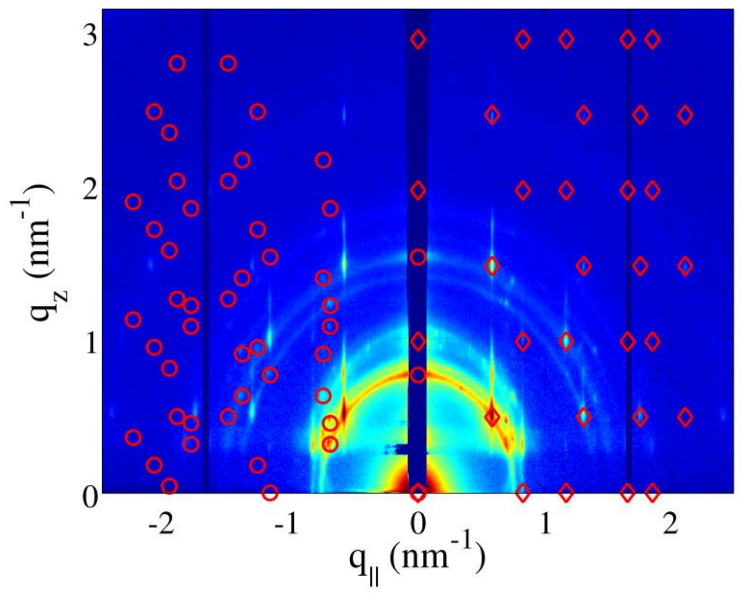
André, A.; Zherebetskyy, D.; Hanifi, D.; He, B.; Samadi Khoshkhoo, M. ; Jankowski, M.; Chasse, T.; Wang, L.-W.; Schreiber, F.; Salleo, A.; Liu, Y.; Scheele, M. Towards Conductive Mesocrystalline Assemblies: PbS Nanocrystals Cross-Linked with Tetrathiafulvalene Dicarboxylate. *Chem. Mater.* **2015**, 27, 8105–8115.

Abstract:

We use the organic semiconductor tetrathiafulvalene dicarboxylate (TTFDA) to assemble PbS nanocrystals into conductive mesocrystals. Density functional theory calculations predict a size-tunable, near-resonant alignment between the PbS 1Sh state and the TTFDA HOMO with the potential to form a conductive channel for holes. We test this hypothesis with transport measurements on TTFDA-functionalized PbS nanocrystals of different sizes and find a pronounced modulation of the field-effect hole mobilities. Photothermal deflection spectroscopy reveals unchanged Urbach energies after ligand exchange, whereas further surface modification by colloidal-atomic layer deposition leads to a strong increase in the density of in-gap states. Hole transport in PbS-TTFDA is unusually robust against such surface modification. Our structural analysis of the mesocrystals suggests that TTFDA induces a defined interparticle spacing, the orientation of atomic lattices and the angle within the mesocrystal unit cell. The results of this work pave the way towards conductive mesocrystalline assemblies of hybrid semiconductor nanostructures with size-tunable transport properties.

The majority of the remaining results have formed the foundation for another manuscript, which is currently under review (submitted on 16/02/2016):

Novak, J.; Banerjee, R; Kornowski, A.; Jankowski, M.; André, A.; Weller, H.; Schreiber, F.; Scheele, M. The Role of Oriented Attachment in the Tetragonal Distortion of PbS Nanocrystal Superlattices and the Occurrence of the Honeycomb Phase. *Submitted.*



In this mansucript, we analyze the structure and morphology of mesocrystalline, body-centered tetragonal (bct) superlattices of PbS nanocrystals functionalized with oleic acid, and the crucial factors which favor an assembly into a honeycomb superlattice of NCs. Our GISAXS measurements taken at ID03 have enabled us to resolve the full 3D structure of superlattices of PbS nanocrystals self-assembled under the conditions specified above. Fitting of the data (**Fig. 1**) revealed a tetragonal distortion and, thus, a bct structure. Lattice parameters were extracted and good agreement with electron microscopy results was obtained.

Figure 1. Typical GISAXS results and fitting of the main reflections.

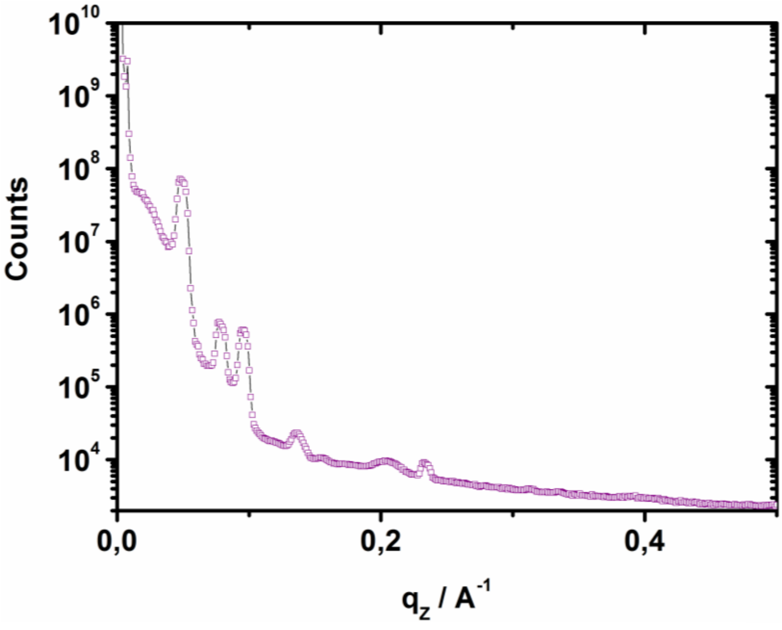


Figure 2. Typical XRR data measured during the beamtine.

The XRR results (**Fig. 2**) have allowed us to determine the preferred orientation of the superlattice normal to the plane. This information has previosuly been unaccessible to us since our preliminary electron microscopy studies could only provide information about the xy-plane, but not in z-direction.

Reflectivity measurements of nanocrystal films are often challenging due to the relatively rough sample surfaces owing to the typically applied "evaporation-induced assembly from solution" (EISA-process). However, our data shows several Bragg peaks, even with higher oder, demonstrating that such measurements are indeed possible on nanoparticle films.

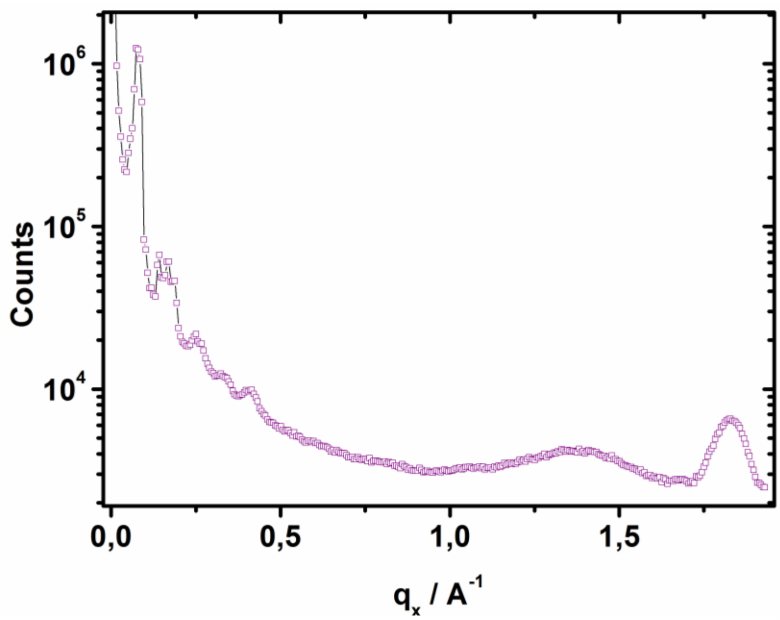


Figure 3. Typical GIXD data measured during the beamtine.

With GIXD, we have not only corroborated our analysis of the GISAXS data, but also revealed valuable new details about the structure of the surfactants which are typically found between the individual nanocrystals of the superlattice: As highlighted in our submitted manuscript, we now have evidence that periodic structures (found around 1.4 A^{-1} in **Fig. 3**) of oleic acid play a pivotal role in the occurrence of a honeycomb lattice of PbS after self-assembly from solution.

Outreach:

Experiment SC-4033 has been highly successful in that 1) one publication has already resulted from the beamtime; 2) another publication is currently under review; 3) our results provide valuable new insights for the controlled design of honeycomb superlattices of nanocrystals which may play an important role for electronics as topological insulators; and 4) our results published in *Chem. Mater.* demonstrate that it is possible to obtain conductive, mesocrystalline superlattices of PbS nanocrystals, which allow for the fabrication of devices consisting of PbS superlattices. These novel materials potentially hold for new optoelectronic properties due to the defined, mutual orientation of the individual nanocrystals. The next step in this direction would be the structural characterization of bilayers of such materials in order to construct more complex device architectures like solar cells or LEDs. Such investigations are the core subject of proposal ref.-nr. 52186, submitted by some of the proposers of the present experiment on 01/03 2016. The results and experience with the material reported on here will greatly facilitate such upcoming studies and ensure their successful execution.