Long-range correlations in a tiny focus.

Unravelling the structural details of mesocrystals by angular X-ray cross-correlation analysis

Ordered arrays of oriented nanocrystals are obtained by directional linking of nanocrystals with organic semiconductor molecules. Detailed knowledge about the structure of the superlattice and its angular correlations with the atomic lattice of the constituting nanocrystals is pivotal in elucidating the relationship between structure and charge transport in these materials. We show how X-ray cross-correlation analysis in combination with a nanofocused X-ray beam rewards such information. This allows for future *in situ* studies of exploiting direction-dependent transport properties in nanocrystal superlattices for optoelectronic applications.

Advances in the synthesis, device fabrication and structural analysis of nanoscale materials have enabled the design and application of "mesocrystals", which are three-dimensional, macroscopic arrays of iso-oriented nanocrystals. In many ways, these nanomaterials mimic classical crystals in which atoms have been replaced by nanocrystals. Mesocrystals play an important role in biology, where their extraordinary structure determines the properties of bones, teeth and sea urchin spines to name only a few examples. Synthetic mesocrystals are already applied and/or currently studied as materials for lighting applications (lasing by photonic crystals) or cloaking devices [1].

The physical properties of mesocrystals are largely determined by their structural coherence, for which the angular correlation between their individual atomic lattice and the underlying superlattice of nanocrystals is a key ingredient. Colloidal nanocrystals stabilized by organic surfactants have been shown to pose excellent building blocks for the design of synthetic mesocrystals with tailored structural properties [2]. Of particular relevance for optoelectronic applications are synthetic mesocrystals with sufficient electronic coupling and charge carrier mobilities. To this end, ligand exchange procedures have been developed to increase the carrier mobilities within the mesocrystal [3]. However, a persisting problem of these protocols is that they are prone to introduce defects in the superlattice structure with some degree of granularity and significantly smaller grain sizes. This poses difficulties in determining the angular correlation between the superlattice and the atomic lattice with a meaningful statistical distribution. Here, we show how angular X-ray cross correlation analysis (XCCA) [4], (for a review, see [5]) in conjunction with a nanofocused X-ray beam can address this problem. Such a method should facilitate the application of synthetic conductive mesocrystals with strong angular correlation for thermoelectrics, spintronics, (magneto-) electronics and optics.

We investigated a conductive mesocrystal on the basis of PbS nanocrystals cross-linked with the organic semiconduc-

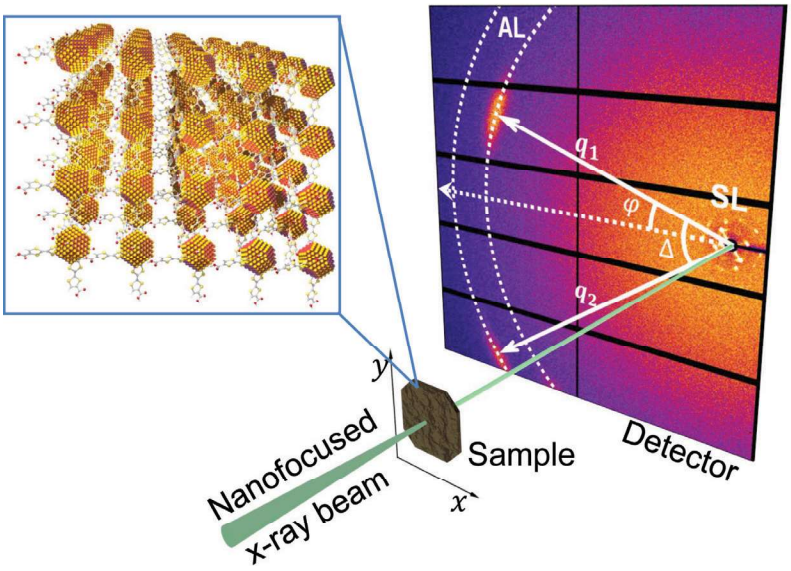

Figure 1

Scheme of the X-ray scattering experiment performed at beamline P10 of PETRA III. Using the large PILATUS 1M detector it was possible to record the scattering signal from both the superlattice (SL) and the atomic lattices (AL) of individual nanocrystals. The inset schematically shows the structure of the mesocrystal consisting of PbS NCs connected by organic ligands.

tor tetrathiafulvalenedicarboxylate (TTFDA). The X-ray scattering experiment was performed at beamline P10 of PETRA III, where the X-ray beam was focused down to about 400 nm. Small-angle X-ray scattering (SAXS) from the nanocrystal superlattice and wide-angle X-ray scattering (WAXS) from the PbS atomic lattice of individual nanocrystals were recorded simultaneously by a large detector positioned behind the sample (Fig. 1). We performed spatially resolved studies of the mesocrystal structure by scanning the sample in the plane perpendicular to the beam, see Fig. 2 (a,b). One can clearly see the granular structure of the sample with typical domain size of about 6-8 μm^2. Interestingly, the same domain structure can be observed in both SAXS and WAXS regions, which indicates that the orientation of the individual nanocrystals is correlated with the orientation of the superlattice.

To analyse this finding in more detail, angular XCCA was applied. This technique is based on the analysis of a two-point angular cross-correlation function between the scattered intensity at two different values of momentum transfer corresponding to scattering from the superlattice and the atomic lattice (Fig. 2c). XCCA revealed that the angular positions of the SAXS diffraction peaks imply a tetragonal distortion along the [001] direction of the superlattice. Therefore, some crystallographic directions are collinear in the atomic lattice of the nanocrystal and the superlattice of the mesocrystal (all three ⟨100⟩ axes as well as the family of ⟨110⟩ directions), while the ⟨111⟩ directions are not (Fig. 2d). Another finding of XCCA is the robust angular correlation between the orientation of the mesocrystal superlattice and individual nanocrystals. The angular disorder between individual nanocrystals was determined to be about 10°, while the average orientation of the nanocrystals coincides with the orientation of the superlattice within the accuracy of few degrees. Such a strong angular correlation preserved over entire domains highlights the mesocrystalline nature of the material.

We anticipate that the future exploration of synthetic mesocrystals with increasing complexity, e.g., binary nanocrystal superlattices, nanorod assemblies, honeycomb lattices, will strongly benefit from the present study. The experiment allows quantifying the structure of the superlattice, its angular correlation with the atomic lattices and the average orientational disorder between atomic lattices simultaneously. In addition, a meaningful statistical distribution of these parameters as well as the length scale of the domains and their boundaries are obtained. This should greatly facilitate the understanding of structure–property relationships in mesocrystals.

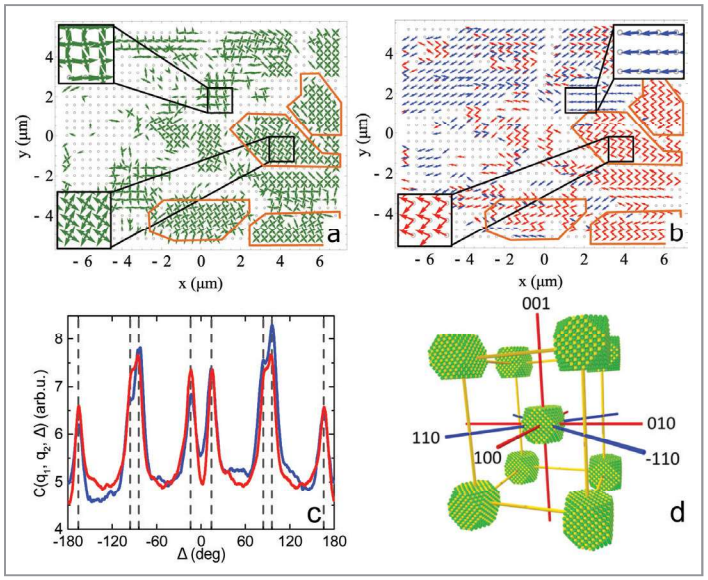

Figure 2

(a) Spatially resolved maps of angular orientation of diffraction peaks of the superlattice (green arrows). (b) Angular orientation of ⟨111⟩ (red arrows) and of ⟨200⟩ (blue arrows) Bragg reflections. Domains are indicated by orange lines. (c) Comparison between the experimentally obtained angular cross-correlation function (blue line) and the model (red line) based on a tetragonal distortion of the mesocrystal superlattice. (d) Schematic of the mesocrystalline unit cell displaying the angular correlation between atomic lattices and the superlattice; collinear axes are indicated in red (⟨100⟩ directions) or blue (⟨110⟩ directions).

Contact: Ivan Vartaniants, ivan.vartaniants@desy.de; Frank Schreiber, frank.schreiber@uni-tuebingen.de; Marcus Scheele, marcus.scheele@uni-tuebingen.de

Authors

Ivan. A. Zaluzhnyy[1,2], Ruslan P. Kurta[3], Alexander André[4], Oleg Y. Gorobtsov[1], Max Rose[1], Petr Skopintsev[1,5], Ilya Besedin[1,2,6], Alexey V. Zozulya[1,3], Michael Sprung[1], Frank Schreiber[4], Ivan A. Vartanyants[1,2] and Marcus Scheele[4]

1. Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany
2. National Research Nuclear University MEPhI, Moscow, Russia
3. European XFEL GmbH, Schenefeld, Germany
4. Eberhard Karls Universität Tübingen, Tübingen, Germany
5. Paul Scherrer Institute, Villigen, Switzerland
6. National University of Science and Technology MISIS, Moscow, Russia

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