

## PbS(OA/TOP)-Mesocrystals: Relationship between Nanocrystal Orientation and Superlattice-Array

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The ability to fabricate nanostructured materials on a large scale *via* a simple and controllable route still remains a challenge for experimentalists. Nevertheless, much progress has been achieved in the provision of potential building blocks. Employing well-established synthetic strategies, nanoparticles with different sizes, shapes and compositions can be readily produced. The strong tendency towards self aggregation and organization of these nano-subunits into superstructures has been used to create mesocrystals with 2D and 3D ordering [1–7]. Such assemblies are normally built up from inorganic nanoblocks which are surface-stabilised by organic molecules. Hence, they combine the properties of the individual nanoparticles with the unique features arising from the collective properties of the ordered arrays. Their properties appear to be promising for a number of potential applications, e.g., biomedical diagnostics, optoelectronics, photonics, photovoltaics and sensors. Lead chalcogenide nanocrystals are especially interesting due to their particular size-dependent tunable optical properties. They exhibit band gaps in the near-infrared region and possess large exciton radii of about 18 nm or even larger. This strong quantization effect makes PbS a prime candidate for applications in the field of infrared optoelectronics such as IR detectors and lasers. In addition, this material is raising attraction for photovoltaic applications since nano-sized PbS has been demonstrated to exhibit multiple exciton generation [8–11].

To date, there are only a few techniques reported for the production of mesocrystals or superstructures. For example, at a defined solvent/non-solvent mixture ratio, PbS nanoparticles self-assemble into macroscopic aggregates resulting in well-ordered mesocrystals. The most common methods for their preparation are the evaporation of the solvent and the addition of a non-solvent, realized with the so-called three-layer supersaturation technique [12–17]. *Talapin et al.* have suggested a mechanism initiated by intrinsic electric dipoles during self assembly [18]. Despite the large number of publications on this topic which appeared in recent years,

there is still no conclusive explanation for the formation processes and/or the nature of the inner structure of these aggregates [19–20]. It has been assumed that the nanoparticles are organized in an ordered manner throughout the whole assembly. However, much of the evidence presented till now has merely depicted the surface structure obtained by SEM. *Nagel et al.*, but also *Rupich et al.* employed SAXS measurements which reveal the *fcc* motif in 3D superstructures [12,14]. On the other hand *Schliehe et al.* examined 2D-ordering within thin sheets [17]. However, no experimental proof is available that the observed ordering is also maintained over the whole volume and not just within the surface of a mesocrystal. Furthermore, in previous studies no relationship of the superlattice and the atomic structure of the individual nanoparticles has been established.

The PbS nano- and mesocrystals were prepared as described by *Nagel et al.* [12]. In this procedure the PbS nanoparticles used for the formation of mesocrystals are stabilised by a mixture of oleic acid (OA) and trioctylphosphine (TOP). The morphology of the PbS mesocrystals was characterized by SEM. Besides regular octahedra, various twinned morphologies and also five-armed star species were found (Fig. 1).

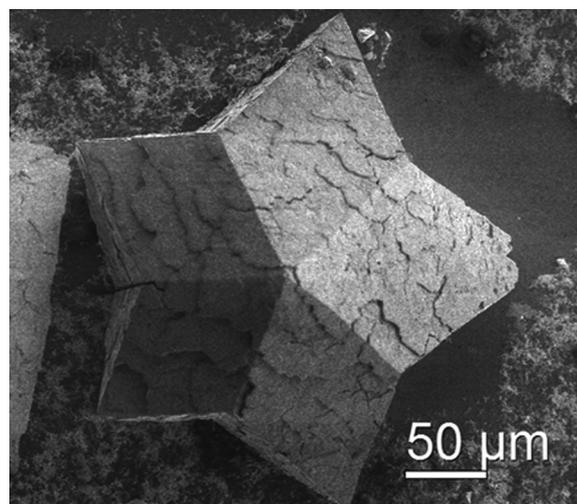


Fig. 1: SEM image of a twinned PbS(OA/TOP) mesocrystal.

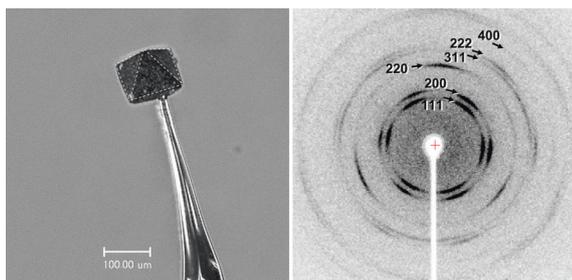


Fig. 2: (right) X-ray diffraction pattern (Mo K $\alpha$  radiation) of an octahedral mesocrystal oriented along its [111] direction, and (left) light microscopy image of the corresponding individual mesocrystal. The mesocrystal consists of a superlattice arrangement of the oriented PbS-nanocrystals stabilized by organic molecules (OA and TOP). For further details see text.

In order to get a first overall impression of the structural ordering effects within the volume of an entire mesocrystal, an octahedral specimen (Fig. 2, left) was chosen for X-ray diffraction investigations. Without going into detail [21], the textured X-ray pattern (Fig. 2, right) can be interpreted as a superposition of diffraction patterns of PbS particles with preferred orientations either nearly along [111] or nearly along  $\langle 110 \rangle$ -orientation; the latter are rotated by  $120^\circ$  with respect to each other. The apparent pseudo-trigonal distribution of the (220) reflections can be explained by absorption effects of the octahedrally shaped mesocrystal.

The inner structure of the PbS mesocrystals was investigated by means of TEM on focused ion beam (FIB) cuts. In this way, artifacts are avoided which might be introduced into the material by conventional diamond cuts. Such defects could be caused by mechanical distortions or swelling of the individuals due to the use of epoxy resin as embedding material. By utilizing a TEM at the middle-resolution regime we obtained three different orientations (recognized as [100], [110] and [111]) of the superlattice which was determined to be cubic (*cf.* below). The superlattice orientations were identified from the fast Fourier transforms (FFTs) of the direct images. The [111] zone (Fig. 3) exhibits hexagonal symmetry and consists exclusively of (220) reflections with lattice spacing  $d_{220} \sim 5.4$  nm, as displayed by the bottom-left inset of Figure 3. By combining the three different zones we found the mesocrystal superstructure to be cubic face-centred with  $Fm\bar{3}m$  symmetry. The unit cell dimension of the superlattice was determined as  $a = 15.4$  nm, which is in good agreement with

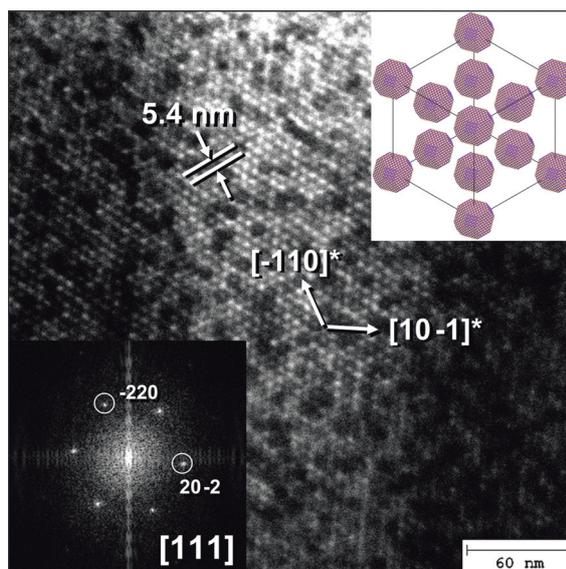


Fig. 3: TEM image (FIB cut) of a PbS(OA/TOP)-mesocrystal showing the closed-packed arrangement (*fcc*) of nanoparticles ([111] zone axis). Bottom left: corresponding FFT; top right: model of the arrangement of nanoparticles within the superlattice.

the expected size for an arrangement of around 5.5 nm-sized PbS nanoparticles stabilized by organic molecules. In addition, the different projections of the superlattice packing of the nanoparticles were simulated. The inset at the right-hand top corner of Figure 3 represents the superlattice-array for the [111] zone.

The individual nanoparticles were investigated by high-resolution TEM (HR-TEM) in order to reveal their habit. By combination of three different projections (along [100], [1-10], and [11-2], Fig. 4, top) we conclude that the habit of a single  $\sim 5.5$  nm-sized particle can be closely approximated by a truncated octahedron (Fig. 4, bottom). The reflections of the FFTs (Fig. 4, middle) have been indexed based on the galena crystal structure  $Fm\bar{3}m$ ,  $a = 5.936$  Å [22,23]).

Furthermore, we applied electron holography on FIB cuts in order to visualize the 3D topography of the superlattice ordering. The measurements were performed at one edge of the cut, from which the platinum shielding was removed. In this way vacuum (empty space) beneath the sample was obtained as needed for the reference wave. The phase micrograph reconstructed from the electron hologram is presented as a 3D-feature in Figure 5. Here, the topography of the sample with the individual nanoparticles is clearly visible. The color code

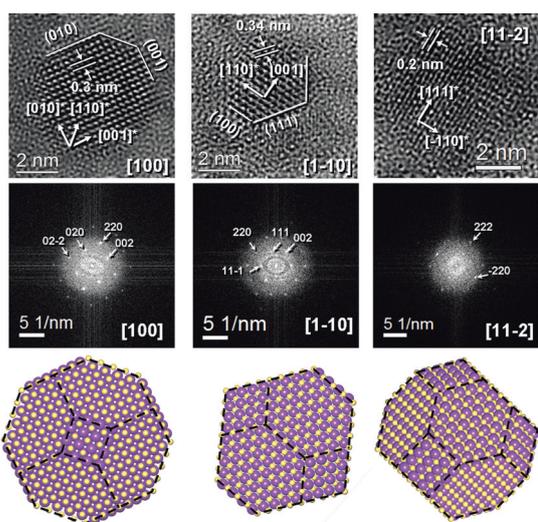


Fig. 4: HR-TEM images of PbS(OA/TOP) nanoparticles (top), corresponding FFTs (middle) and particle simulations (bottom; from left to right: projections along the zone axes [100], [1-10], [11-2]).

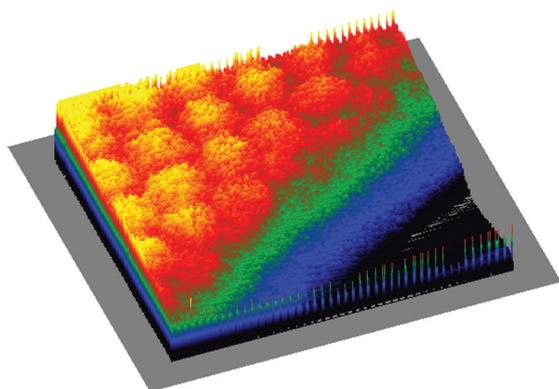


Fig. 5: Reconstructed phase image (3D representation) of the electron hologram taken from the FIB cut of a PbS(OA/TOP) mesocrystal. Color code: yellow to orange represent steps of  $\sim 4$  nm thickness.

from yellow to orange indicates a height of about 4 nm. The value of 8 nm corresponds to the size (thickness) of a single nanoparticle along with its organic shell. This value was calculated from the measured phase shift which is proportional to the mean inner potential of PbS for electrons (17.19 V [24]), the thickness and a constant (0.0073 1/V nm) related to the microscope. Electron holography is a powerful tool to image nanosized electrical and magnetic fields [25,26]. Nonetheless, the predicted existence of intrinsic electric dipole fields around the PbS nanoparticles [18] could not be evidenced.

The present contribution is restricted to prelimi-

nary results obtained by means of X-ray and electron diffraction, high-resolution TEM and electron holography. More detailed investigations concerning nanoparticle orientations, the “real” symmetry of the superlattice and the formation of domains within the mesocrystals are in progress.

## References

- [1] S. A. Harfenist, Z. L. Wang, M. M. Alvarez, I. Vezmar, and R. L. Whetten, *J. Phys. Chem.* **100** (1996) 904.
- [2] Z. L. Wang, *Adv. Mater.* **10** (1998) 13.
- [3] E. V. Shevchenko, D. V. Talapin, A. Kornowski, F. Wiekhorst, J. Kötzler, M. Haase, A. Rogach, and H. Weller, *Adv. Mater.* **14** (2002) 287.
- [4] E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien, and C. B. Murray, *Nature* **439** (2006) 55.
- [5] H. Cölfen, and M. Antonietti: “Mesocrystals and Nonclassical Crystallisation” Wiley (2008).
- [6] R. K. Mallavajula, and L. A. Archer, *Angew. Chem. Int. Ed.* **50** (2011) 578.
- [7] Z. N. Zhu, H. F. Meng, W. J. Liu, X. F. Liu, J. X. Gong, X. H. Qiu, L. Jiang, D. Wang, and Z. Y. Tang, *Angew. Chem. Int. Ed.* **50** (2011) 1593.
- [8] R. Vogel, P. Hoyer, and H. Weller, *J. Phys. Chem.* **98** (1994) 3183.
- [9] S. A. McDonald, G. Konstantatos, S. Zhang, P. W. Cyr, E. J. D. Klem, L. Levina, and E. H. Sargent, *Nat. Mater.* **4** (2005) 138.
- [10] G. Konstantatos, I. Howard, A. Fischer, S. Hoogland, J. Clifford, E. Klem, L. Levina, and E. H. Sargent, *Nature* **442** (2006) 180.
- [11] A. L. Rogach, A. Eychmüller, S. G. Hickey, and S. V. Kershaw, *Small* **3** (2007) 536.
- [12] M. Nagel, S. G. Hickey, A. Fromsdorf, A. Kornowski, and H. Weller, *Zeitschr. Phys. Chem. - Int. J. Res. Phys. Chem. & Chem. Phys.* **221** (2007) 427.
- [13] D. V. Talapin, E. V. Shevchenko, M. I. Bodnarchuk, X. C. Ye, J. Chen, and C. B. Murray, *Nature* **461** (2009) 964.
- [14] S. M. Rupich, E. V. Shevchenko, M. I. Bodnarchuk, B. Lee, and D. V. Talapin, *J. Am. Chem. Soc.* **132** (2010) 289.
- [15] P. Podsiadlo, G. Krylova, B. Lee, K. Critchley, D. J. Gosztola, D. V. Talapin, P. D. Ashby, and E. V. Shevchenko, *J. Am. Chem. Soc.* **132** (2010) 8953.
- [16] J. Akhtar, M. A. Malik, P. O'Brien, and M. Helliwell, *J. Mater. Chem.* **20** (2010) 6116.
- [17] C. Schliehe, B. H. Juarez, M. Pelletier, S. Jander, D. Greshnykh, M. Nagel, A. Meyer, S. Foerster, A. Kornowski, C. Klinke, and H. Weller, *Science* **329** (2010) 550.
- [18] D. V. Talapin, E. V. Shevchenko, C. B. Murray, A. V. Titov, and P. Kral, *Nano Lett.* **7** (2007) 1213.
- [19] E. S. Bozin, C. D. Malliakas, P. Souvatzis, T. Proffen, N. A. Spaldin, M. G. Kanatzidis, and S. J. L. Billinge, *Science* **330** (2010) 1660.

- [20] *D. A. Walker, B. Kowalczyk, M. O. De la Cruz, and B. A. Grzybowski, Nanoscale, DOI: 10.1039/C0NR00698J.*
- [21] *P. Simon, I. A. Baburin, R. Cardoso-Gil, W. Carrillo-Cabrera, A. Eychmüller, S. G. Hickey, L. Liebscher, E. Rosseeva, and R. Kniep, in preparation.*
- [22] *L. S. Ramsdell, Amer. Mineral. 10 (1925) 281.*
- [23] *J. H. Wernick, Amer. Mineral. 45 (1960) 591.*
- [24] *M. Gajdardziska-Josifcska, A. H. Carim in: E. Völkl, L. F. Allard, and D. C. Joy (Eds.): "Introduction to Electron Holography" Kluwer Academic/ Plenum Publishers, New York (1999) 267.*
- [25] *H. Lichte, and M. Lehmann, "Electron holography - basics and applications" Reports on Progress in Physics 71 (2008) 016102.*
- [26] *H. Lichte, P. Formanek, A. Lenk, M. Linck, C. Matzeck, M. Lehmann, and P. Simon, Ann. Rev. Mater. Res. 37 (2007) 539.*

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