Functional Materials

MS.3.P064
The structure of supercrystals made by self-assembled nanoscaled Ag_2S hollow spheres and Ag_2S nanodiscs

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Keywords: Transmission electron microscopy, superscrystals, hollow spheres, nanodiscs

Supercrystals consisting of highly periodic arrangements of monodisperse nanoparticles were intensely investigated in the recent past due to their unique properties, which can differ from those of individual nanoparticles and bulk compounds [1]. For example, semiconductor and precious metal nanoparticles were utilized as so-called artificial atoms for a variety of functional superstructures [2]. While a reasonable number of 3D supercrystals were built with different types of massive nanoparticles, including Ag_2S, nanoscale hollow spheres have not been used as building blocks until now. In this work we study the structure of supercrystals which consist of nanoscale Ag_2S hollow spheres (HS) and Ag_2S nanodiscs (ND).

For the structural characterization we used scanning electron microscopy (SEM), high-resolution (HR) transmission electron microscopy (TEM), selected-area electron diffraction (SAED) and high-angle annular dark-field (HAADF) scanning TEM (STEM). The HSs and NDs were obtained by a microemulsion approach [3]. Samples for electron microscopy were prepared by evaporating ethanol-based suspensions on an amorphous carbon film. SEM was performed on a Zeiss Supra 40 VP equipped with a field emission gun (acceleration voltage 4–20 kV, working distance 3 mm). HRTEM and SAED were conducted on a Philips CM 200 FEG/ST at 200 kV, while HAADF-STEM images are taken with an aberration-corrected FEI Titan^3 80-300 at 300 kV.

In the following, the properties of supercrystals consisting self-assembled Ag_2S HSs and individual Ag_2S HSs are described. TEM (Fig. 1 a) and HAADF-STEM (Fig. 1b) images clearly evidence the hollow sphere structure of Ag_2S nanoparticles with an average outer diameter of ~ 37 nm, a wall thickness of ~ 10 nm and an inner cavity diameter of ~ 17 nm. Lattice fringes extend through the whole hollow sphere (image not shown here) indicate the single crystalline structure of the sphere wall. The measured fringe distance of 2.8) Å is compatible with d$(\bar{1}12)$ =2.84 Å in monoclinic α-Ag_2S/acanthite. The structure and composition of Ag_2S HSs is further confirmed by SAED, which demonstrates the presence of α-Ag_2S (Fig. 1c). The Ag_2S HS supercystals show regularly assembled building blocks (i.e. individual nanoscaled Ag_2S HSs) with a dense packing of hard spheres and overall dimensions of 10–30 micrometers (Fig. 1d). Herein, the individual Ag_2S hollow spheres are clearly visible (Fig. 1e,f).

Large tube-like supercrystals of 5–30 µm in length and about 500 nm in diameter are formed by self-assembling of Ag_2S NDs. Fig. 2a displays a side-view of a single tube-like supercrystal. Top-views of Ag_2S nanodisc arrays show a tube-like structure with an outer diameter of 400–500 nm and a lens-shaped inner channel with dimensions of about 200 nm x 50 nm (Fig. 2b). The TEM image in Fig. 2c clearly indicates the substructure of the nanodisc supercrystal. Accordingly, the tube-like superstructure is composed of individual nanodiscs that are deposited on top of each other. Notably, the parallel rows of stacked nanodiscs are slightly twisted along the longitudinal axis of the supercrystal resulting in a helix-like winding. Assuming that such winding increases the structural stability of the nanodisc assembly, its direct consequence is the presence of an inner channel, thus, a tube-like structure. According to Fig. 2c) and d), the nanodiscs are characterized by an average diameter of ~ 20 nm and a thickness of ~ 7 nm as schematically depicted in Fig. 2e. The HRTEM image in Fig. 2d illustrates the structure of a single Ag_2S nanodisc in detail. Lattice fringes across the whole nanodisc confirm the single crystallinity of the nanodiscs. The measured fringe distance of 2.4 Å is again compatible with the presence of monoclinic α-Ag_2S/acanthite (d(121) =2.44 Å). SAED patterns recorded from single nanodisc supercrystals indicate a remarkably high intensity of the $(\bar{1}12)$ reflection (Fig. 2f) which is preferentially aligned along a particular direction indicating a textured alignment of the disks. The high peak intensity of $(\bar{1}12)$ is also evident when comparing the SAED of nanodiscs with that of hollow sphere supercrystals (Fig. 2f and Fig. 1c). Since the single crystalline nanodiscs are well-assembled along the longitudinal axis of the tube-like supercrystal such a textural effect is not a surprise and can be explained assuming that the $(\bar{1}12)$ planes are parallel to the surface of the nanodiscs (scheme Fig. 2e). The orientation of the nanodiscs is also in agreement with the (121) lattice fringes in the HRTEM image Fig. 2d, because (121) is almost perpendicular to $(\bar{1}12)$

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4. This work has been performed within the projects C1.4 and C4.5 of the DFG Research Center for Functional Nanostructures (CFN). It has been further supported by a grant from the Ministry of Science, Research and the Arts of Baden-Württemberg (Az: 7713.14-300).

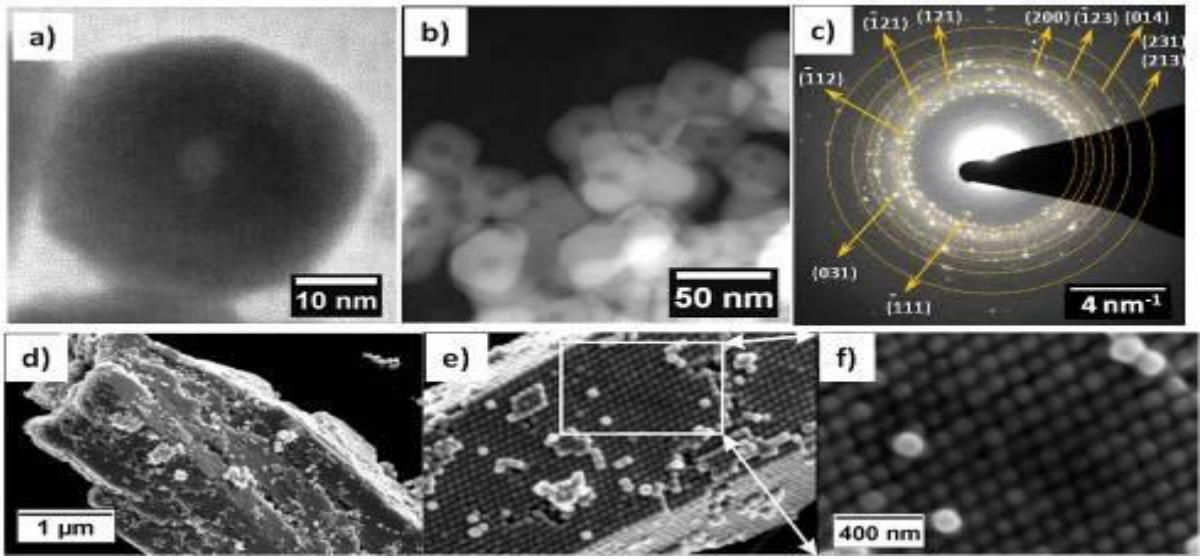

Figure 1. (a) HRTEM and (b) HAADF-STEM images of single Ag_2S HSs; (c) indexed SAED pattern of Ag_2S supercrystals (Miller indices correspond to bulk monoclinic α-Ag_2S/acanhite); (d) overview SEM image and (e,f) detail SEM images of Ag_2S hollow sphere supercrystals showing the dense packing of hollow spheres.

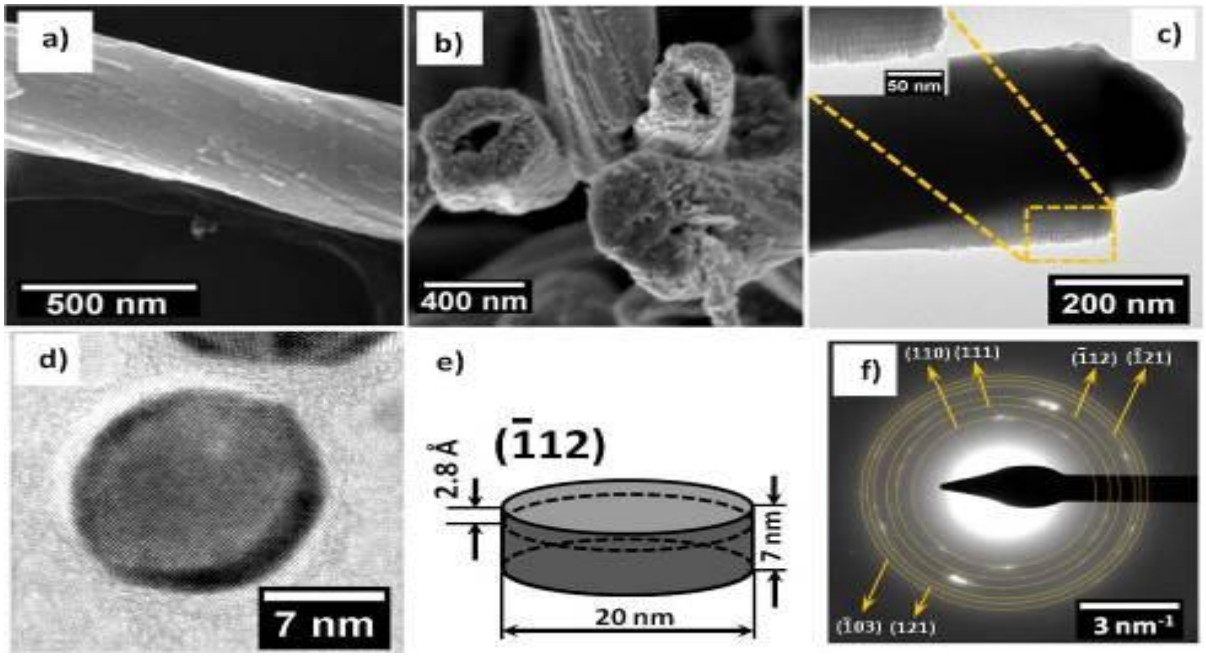

Figure 2. (a) Side-view and (b) top-view SEM images of Ag_2S nanodisk supercrystals; (c) TEM image showing stacked nanodiscs; (d) HRTEM and (e) schematic representation of a single Ag_2S ND; (f) indexed SAED pattern of Ag_2S ND supercrystals, which shows a strong $(\bar{1}12)$ texture (Miller indices correspond to bulk monoclinic α-Ag_2S/acanhite).