The structure of supercrystals made by self-assembled nanoscaled Ag_2S hollow spheres and Ag_2S nanodiscs

R. Popescu[1], P. Leidinger[2], C. Feldmann[2] and D. Gerthsen[1]

[1] Laboratorium für Elektronenmikroskopie, Karlsruhe Institute für Technology (KIT), Engesserstr. 7, D-76131 Karlsruhe, Germany
[2] Institut für Anorganische Chemie, Karlsruhe Institute für Technology (KIT), Engesserstr. 15, D-76131 Karlsruhe, Germany

Motivation

- Synthesis of supercrystals consisting of highly periodic arrangements of monodisperse nanoparticles
- Nanoparticle superlattices with interesting optical and catalytic properties [1] and semiconductor and precious metal NPs used as so-called artificial atoms for a variety of functional superstructures [2]
- Preparation of well-ordered 2D and 3D NP assemblies is still a challenge in chemistry and materials science
- Nanocrystal superlattices consisting of nanoscale Ag_2S hollow spheres (HS) and Ag_2S nanodiscs (ND) as building blocks are synthesized and investigated for the first time

[1] a) M. P. Pileni, *J. Colloid Interface Sci.* **388** (2012), 1 ;
b) S. M. Rupich, D. V. Talapin, *Nature Mater.* **10** (2011), 815.
[2] a) Z. Lu, Y. Yin, *Chem. Soc. Rev.* **41** (2012), 6874 ;
b) R. C. Ashoori, *Nature* **379** (1996), 413.

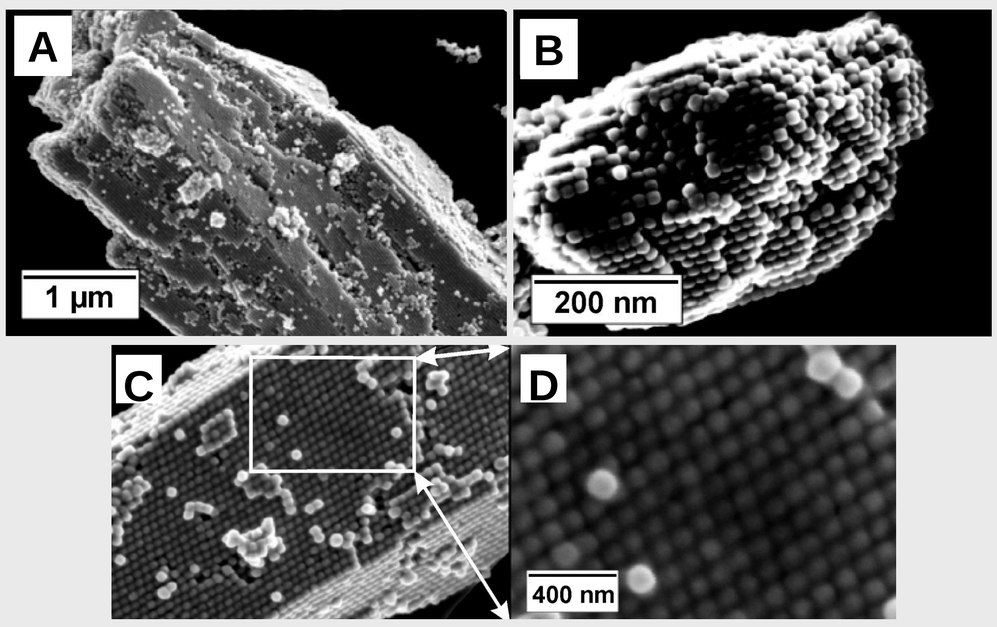
Experimental Details

- Ag_2S (acanthite) HSs and NDs prepared by microemulsion approach [3]
- Structural characterization by:
  - High-resolution (HR) transmission electron microscopy (TEM) and selected-area electron diffraction (SAED)
    Philips CM200 FEG/ST at 200 keV
  - Scanning electron microscopy (SEM)
    Zeiss Supra 40 VP equipped with a field emission gun (acceleration voltage 4–20 kV, working distance 3 mm)

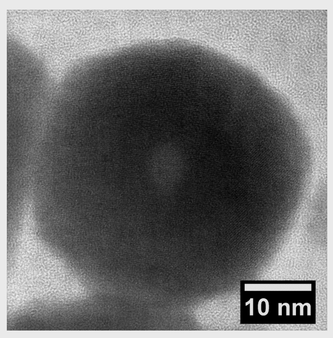
[3] D. H. M. Buchold and C. Feldmann, Adv. Funct. Mater. **18** (2008), 1002

Results

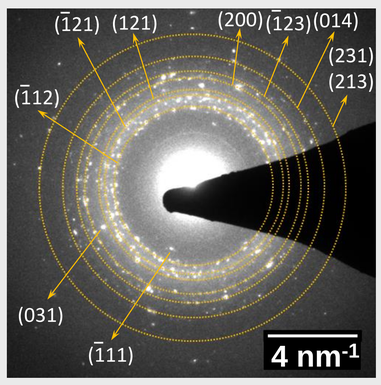
Nanoparticale superlattices with Ag_2S hollow spheres as building blocks



- (A-D) SEM images of Ag_2S supercrystals



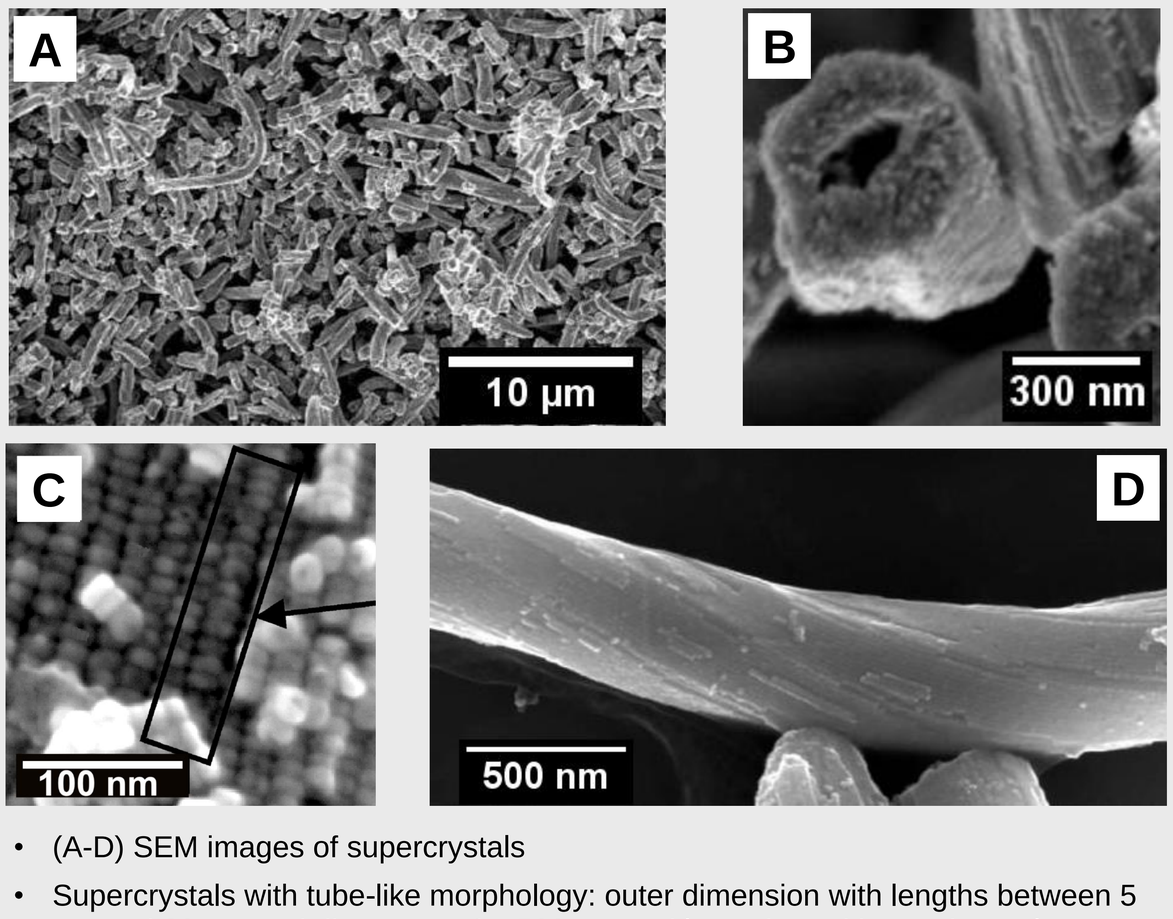
- TEM image of single NP with hollow sphere morphology



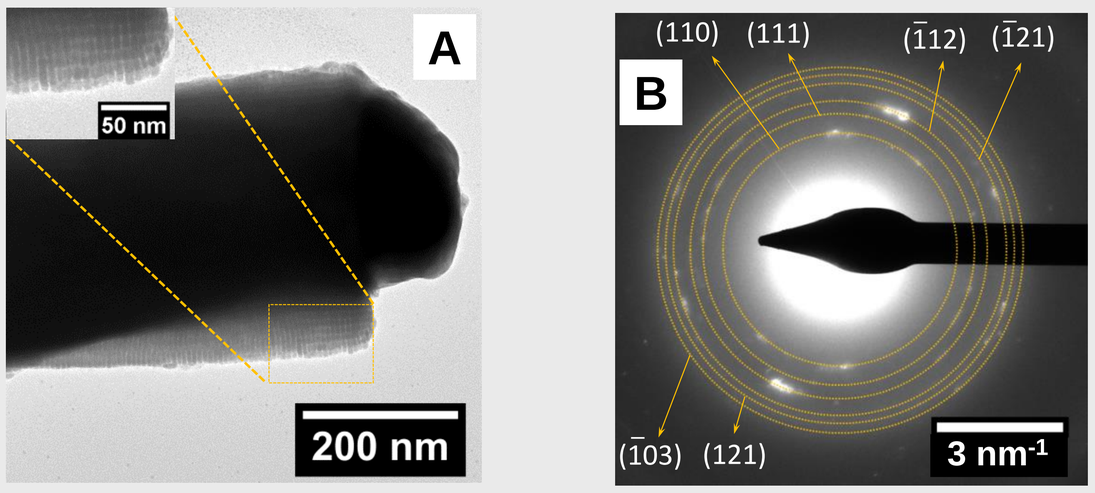
- SAED: monoclinic α-Ag_2S structure

- Supercrystals with 10-30 µm overall size formed by densely packed spherical Ag_2S hollow spheres with a narrow size distribution
- Monoclinic α-Ag_2S with acanthite structure (Spacegroup P21/n)

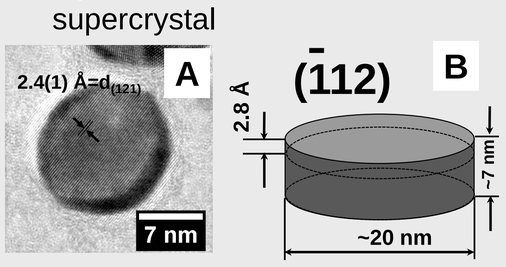
Nanoparticle superlattices with Ag_2S nanodisks as building blocks



- (A-D) SEM images of supercrystals
- Supercrystals with tube-like morphology: outer dimension with lengths between 5 µm and 30 µm and diameters of ~ 500 nm and lens-shaped inner channel
- Supercrystals composed of nanodisks with narrow size distribution
- Stacked nanodisks in rows (almost) parallel to the tube axis



- (A) TEM image and (B) SAED pattern of electron transparent region of supercrystal with remarkably high intensity of (1̄12) reflection.
- Texture explained assuming that (1̄12) is parallel to the predominant layer of single crystalline NDs which are well-assembled along the longitudinal axis of the tube-like supercrystal



- (A) HRTEM image (lattice-fringe distance 2.4(1) Å=$d_{(121)}$) (B) scheme of crystallographic orientation of nanodisk
- (121) lattice fringes on HRTEM image support the assumed (1̄12) orientation of NDs, because (121) is almost rectangular to (1̄12)

Summary

- Nanoparticle superlattices with dimensions in the micrometer range formed by Ag_2S hollow spheres (outer diameter: ~37 nm; wall thickness: ~10 nm) and Ag_2S nanodisks (diameter: ~20 nm; thickness: ~7 nm) as building blocks
- Within nanocrystals, Ag_2S HSs arranged similar to the close packing of hard spheres, while Ag_2S nanodiscs are stacked to parallel rows forming a tube-like superstructure with a helix-like winding
- Microemulsion approach a useful option for obtaining further nanocrystal superlattices

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