

NOVEL ANISOTROPIC NANOPARTICLES

R. Nesper¹ G. Patzke F. Krumeich
Chemistry Dept. ETH Zuerich Laboratory of Inorganic Chemistry ZUERICH
CH-8092 SWITZERLAND

Nanoparticles will become an important factor in the scale-down attempts of future technologies. However, there is a need for a toolbox for applying such materials in a flexible and creative way. Anisotropic nanomaterials may play here a key role because they exhibit morphological prefunctionalizations which allow for new physical effects, elegant orientation techniques, and morphological design of functional nanoparticles. We are concentrating on oxidic nanotube and nanofiber materials by developing reliable synthesis procedures, characterization techniques and application pathways. There is a growing need for synthetic guidelines that can be applied on the preparation and tailoring of nanomaterials. Systematic studies reveal that some elementary synthetic parameters like selection of inorganic ionic additives and solvent control of temperature as well as reaction times allow for the design of novel transition metal oxide nanorods via flexible high-quality solvothermal syntheses [1, 2]. Furthermore, all these preparative advantages can be customized again by variation of additive concentration, reaction time and temperature of a standard procedure. Thus, a large selection of synthetic tools has been established: a precise approach to oxidic nanorods with desired compositions and aspect ratios.

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CdSe CLUSTER MOLECULES. SYNTHESIS, STRUCTURE AND OPTICAL PROPERTIES

A. Eichhoefer¹ D. Fenske² U. Banin³ V. Soloviev⁴ A. Aharoni⁵
Forschungszentrum Karlsruhe Institute of Nanotechnology
Forschungszentrum Karlsruhe, Institute of Nanotechnology P.O. Box 3640
KARLSRUHE 76021 GERMANY

Size dependent electronic and optical properties manifesting quantum confinement effects have been studied extensively for larger nanocrystals, spanning the size range of 2 to 10 nm. Cluster-molecules of semiconductor materials, composed of tens of atoms with bonding resembling that present in the solid state, are in this respect interesting molecular models for the bulk. Therefore we recently extended the investigation of size dependence effects also to CdSe cluster-molecules that represent an ultimate molecular limit for the semiconductor. The largest cluster with 32 Cd atoms, already overlapped in size with the smallest CdSe nanocrystals prepared via colloidal synthesis. The absorption onset of the clusters showed a systematic shift to smaller wavelength with reduced size manifesting the quantum confinement effect, continuing the dependence observed for larger CdSe nanocrystals. The emission in all cluster-molecules is observed only at low temperature and is red-shifted significantly from the absorption onset. Further characteristics of the emission like lifetimes in the msec range and the temperature dependence strongly suggest that emission can be assigned to optically forbidden transitions involving surface states of the emission. While all these measurements were run on oil mulls of the crystalline powders of the clusters additional investigations like UV-Vis, dynamic light scattering and FT mass spectrometry target the behavior and the properties of these cluster molecules in solution.

Keywords: CLUSTER MOLECULES, OPTICAL SPECTROSCOPY, SINGLE CRYSTAL XRD

MoS₂ NANOTUBE SELF-ASSEMBLIES

M. Remskar^{1,2} A. Mrzel¹ F. Levy²
¹J. Stefan Institute, Solid-State Physics Department, Jamova 39, SI-1000 Ljubljana, Slovenia ²Institut de Physique de la Matière Complexe, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

The chemical transport reaction was found as a successful technique for synthesis MoS₂ and WS₂ inorganic nanotubes. The nearly equilibrium conditions enable the growth of nanotubes up to several millimeters lengths with low density of structural defects [1]. The MoS₂ and WS₂ micro and nanotubes have been successfully alloyed with gold and silver. The characteristic tubular structure stabilizes the compounds, which are not stable in the flat geometry. Lattice expansion perpendicular to the basal plane removes the tube chirality and causes a preferable growth mode in form of coaxial cylinders. The suppression of the tendency for the self-assembly of the alloyed nanotubes can be explained by the axial rotation of the nanotubes at elevated temperatures [2].

The narrowest single wall nanotubes with diameters below one nanometer have been synthesized in macroscopic quantities using the catalyzed transport reaction using C₆₀ [3] or C₇₀ molecules as a growth promoter. The nanotubes, which are up to hundreds of microns long, display a self-assembly into various regular geometrical shapes on different length scales. They group to bundles composed of few nanotubes up to several hundreds thousands nanotubes forming the molecular crystal with hexagonal symmetry. The bundles can easily decompose to narrow assemblies and even to individual nanotubes. Here we report on electron microscopy of nanotube assemblies and on scanning tunneling microscopy of an individual MoS₂ nanotube.

References

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STRUCTURE STUDY OF NANOSIZED FERRITES

Z. Somogyvari¹ E. Svab¹ Gy. Meszaros¹ K. Krezhov² I. Nedkov³ I. Sajo⁴ F. Bouree⁵

¹Research Institute for Solid State Physics and Optics Konkoly Thege St 29-33 BUDAPEST 1121 HUNGARY ²Institute for Nuclear Research and Nuclear Energy, Bulg. Acad. Sciences ³Institute of Electronics, Bulg. Acad. Sciences ⁴Institute of Chemistry, Hun. Acad. Sciences ⁵Laboratoire Leon Brillouin (CEA-CNRS)

With the recent advances in nanotechnology, ferrites became of considerable current interest, as they exhibit altered magnetic behavior, due to surface and size effects and interparticle interactions.

In this study we focused our interest on the crystallographic and magnetic ordering of various nanosized ferrites, prepared by the soft chemistry method. Magnetite (Fe₃O₄, *Fd-3m*) samples with grain sizes down to 15 nm were studied, serving as a basis of our systematic investigation. The different dependency of the magnetization of the two ferrimagnetically coupled sublattices and the slight changes of the first neighbor Fe-O distances were established. The vacancy distribution in nanocrystalline needle shaped maghemite (γ -Fe₂O₃) particles with average size 240 nm x 30 nm was determined from multiprofile Rietveld analysis of neutron and X-ray diffraction patterns. We have shown, that the ordering of vacancies results in the formation of a tripled unit cell with space group *P4₁2₁2* even at this small particle size. The refined interatomic distances and the tetragonal distortion of the lattice are in good agreement with the vacancy distribution. The influence of grain sizes in the 10 nm -1 μ m range on the local atomic and magnetic parameters were investigated for BaFe_{12-2x}(CoTi)_xO₁₉ (x = 0.45-0.85). The anisotropy of the thermal expansion coefficient along the hexagonal axis (*P6₃/mmc*) was established. The cation distribution and the sublattice magnetization were determined. The reduction of the sublattice magnetic moments and the appearance of diffuse scattering indicated short ranged magnetic noncollinearity.

Keywords: FERRITES, NANOCRYSTALLINE, RIETVELD REFINEMENT