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Abstract

“Controlled transformations of organozinc precursor systems towards semiconductor nanocrystals”

Author: Aleksandra Borkenhagen

Supervisor: prof. Janusz Lewiński

Although numerous synthetic strategies for nanomaterials have been developed to meet increasing demand, scalable and environmentally sustainable approaches remain a significant challenge. To date, most conventional liquid-phase synthetic methods for producing high-quality semiconductor nanocrystals typically require elevated temperatures, expensive solvents, multistep purification processes, and sophisticated stabilizing ligands. In contrast, solid-state chemical transformations offer potential advantages by eliminating the need for solvents and additional stabilizing ligands. However, due to the relatively low reactivity and diffusion rates of chemical species in the solid-state, nanocrystal nucleation and growth are substantially limited. To overcome these energy barrier, thermal and/or mechanical treatment are typically required, making these systems energetically less feasible.

This dissertation introduces a novel all-solid-state synthetic approach for semiconductor nanocrystals that operates under ambient conditions without external energy input. This strategy relies on rationally designed organozinc solid-state precursor based on $[(L)ZnR]_n$ -type molecular clusters, incorporating reactive Zn–C and Zn–N bonds confined within a single-crystal lattice prone to water-mediated hydrolysis.

The first part of the thesis describes design and synthesis of a model solid-state precursor of quantum-sized ZnO nanocrystals. As the model system, the tetranuclear ethylzinc benzamide cluster, $[(BA)ZnEt]_4$, was synthesized and isolated as single crystals, providing a well-defined precursor system to investigate solid-state transformations to semiconductor nanocrystals. This predesigned precursor is reactive towards selected atmospheric components and, upon exposure to air, enables efficient growth of nanocrystals within its own crystalline yet dynamic body, which is prone to rearrangements, thereby overcoming the limitation of efficient mass transport in the solid-state.

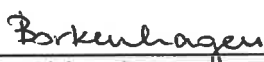
To explore the transformation processes at the molecular and nanoscale levels, the second part of the thesis employs a wide range of time-resolved in situ and ex situ characterization methods, including absorption, vibrational, and nuclear magnetic spectroscopies, various diffraction methods, microscopy, and thermal analysis. These comprehensive studies unveil the formation of nanocrystals and their

aggregation within the crystalline precursor, as well as within emerging amorphous matrix—an aspect that has remained largely unexplored in solid-state chemistry. Notably, the results highlight the critical role of water molecules in initiating the hydrolysis of $[(BA)ZnEt]_4$ clusters and the formation of intermediate zinc oxo/hydroxo species alongside the amorphous matrix, which facilitates efficient mass transport and enabling efficient crystal growth in a solid-state environment.

The third and fourth part of the thesis demonstrate the versatility of the presented system. The volatile under vacuum organic matrix based on hydrolysed BA-H ligands, is effectively removed through vacuum-triggered sublimation without using solvents, high temperatures, or complicated surface area activation procedures, yielding a nanocrystalline mesoporous scaffold of semiconductor building blocks. Furthermore, the presented solid-state $[(BA)ZnEt]_4$ precursor system was successfully extended to other hydrolytic agents. Specifically, hydrogen sulfide was employed as an alternative hydrolytic agent, leading to the successful formation of ZnS nanocrystals, thus confirming the greater scope of the presented system.

The fifth part of the thesis describes complementary studies on water- and water/dioxygen- mediated transformations of the $[(BA)ZnEt]_4$ precursor in solution, using in situ ^1H NMR spectroscopy. These studies provide not only valuable insights into the reactivity of the model precursor in solution but also highlight significant differences between the processes occurring in the solid-state and those in solution. These results reveal that the reaction pathways in solution depend on the oxygen source used—either a mixture of dioxygen and water (from air) or water alone—whereas in the solid-state, the process is highly selective towards water.

In summary, this dissertation contributes to the development of innovative materials synthesis, addressing the ongoing challenge of developing sustainable synthetic strategies. It presents a simple, cost-effective, and energy-efficient method for producing high-quality semiconductor nanocrystals. Notably, the reported system not only demonstrates, for the first time, the formation of nanocrystals under ambient conditions without the need for external stimuli, but also provides comprehensive molecular-level insights into complex solid-state transformation mechanisms through a range of time-resolved in situ techniques.


Aleksandra Borkenhagen