



Fundamentals of nanocrystal formation

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Research on the controlled formation of nanocrystals, or nanocrystalline materials, has reached an overwhelming extent in recent years. The complexity of the investigated systems has steadily increased, with numerous examples of composite systems consisting of three, four or even five compounds combined at the nanoscale. However, preparative strategies are developed in an empirical manner in the vast majority of reports, and rational approaches for the controlled formation of nanomaterials – even consisting of only a single compound – are available for merely a limited number of systems. Consequently, understanding of the fundamental mechanisms of nanocrystal formation and growth is only slowly increasing, though most synthetic approaches are based on one of a few general types. Most popular are precipitation reactions, reduction syntheses, hydrothermal and solvothermal approaches, and aqueous and non-aqueous sol-gel reactions as liquid phase methods, complemented

by flame pyrolysis as a gas phase method, as well as high-temperature powder routes. A mechanistic understanding of the formation of nanocrystals in these approaches, however, is key to their rational design and thus the controlled preparation of desired structures and morphologies. In recent years, significant advances have been made in the study of nanocrystal formation, particularly by the use of advanced analytical tools, revealing a complex interplay between chemistry and physics. Therefore, an important task for the future is the consolidation of the numerous insights into the formation processes for different systems in order to obtain a generalized picture of nanocrystal formation and to develop predictive models.

In this themed issue, we have combined cutting edge research from groups around the world, with a focus on novel insights and fundamental studies on the formation of nanocrystals, including amorphous intermediates, in both liquid and gas phase systems. We are very happy about the positive resonance, with 16 research articles and 7 communications as well as 3 highlight articles in this themed issue.

Two studies are devoted to gas phase systems: Schulz *et al.* elucidated the first reaction steps in the formation of iron oxide nanoparticles during flame synthesis from Fe(CO)₅ as precursor, employing *e.g.* a quartz crystal microbalance setup for concentration

measurements, as well as CFD simulations (DOI: 10.1039/C5CE00456J). Mädler *et al.* studied the formation of WO₃ nanoparticles during flame spray pyrolysis by means of *in situ* XRD and HRTEM measurements in combination with atomistic modeling (DOI: 10.1039/C5CE00526D).

The majority of articles are devoted to the study of liquid phase systems. In several reports, cutting-edge *in situ* analytical techniques were employed. Koziej *et al.* combined *in situ* XANES analyses with UV-vis and IR data to obtain broad insights into the formation and growth mechanism of Cu-based nanoparticles, linking the organic and inorganic reactions in solution (DOI: 10.1039/C5CE00454C). Iversen *et al.* performed *in situ* total X-ray scattering studies to elaborate details of the structure of intermediates during the hydrolytic formation of anatase nanoparticles (DOI: 10.1039/C5CE00544B).

Several manuscripts are focused on metal nanoparticles and nanostructures. Polte provides a personal perspective on the formation of metal nanocrystals, postulating a strong connection between crystal growth and colloidal stability (DOI: 10.1039/C5CE01014D). Lee and co-workers report the formation of CuIr alloy nanocrystals with gradient composition (DOI: 10.1039/C5CE00061K), as well as the regio-specific growth of Au on PtZn nanocubes, enabling the formation of octapods (DOI: 10.1039/C5CE00429B). Furthermore, his group has contributed

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two studies on the formation of complex Pt-based nanostructures, PtCu@Ru nanorattles (DOI: 10.1039/C5CE00398A), as well as dendritic structures (DOI: 10.1039/C5CE00438A). A study on the formation mechanism of core–double shell nanoparticles is provided by Maenosono *et al.* (DOI: 10.1039/C5CE00394F), whilst Tsuji *et al.* (DOI: 10.1039/C5CE00357A) present the use of Au nanorods as sacrificial templates for the formation of frame-like Rh nanorods. A detailed investigation of structural evolution during the galvanic replacement reaction of silver nanoparticles in organic media was conducted by Collins *et al.* (DOI: 10.1039/C5CE00659G).

Other works are devoted to the rational design of functional materials: the highlight article of Steunou and Livage provides a thorough overview of the recent achievements in the synthesis of 1-D vanadium pentoxide and vanadate nanostructures, including fascinating examples of belt- and ring-like structures (DOI: 10.1039/C5CE00554J). On the other hand, Garnweitner *et al.* (DOI: 10.1039/C5CE00629E) investigated the formation of Al-doped ZnO nanocrystals, showing that the morphologies can be tuned by proper control of the surface chemistry. Furthermore, Yu *et al.* (DOI: 10.1039/C4CE02228A) report a green method and provide a mechanistic explanation for the generation of hierarchical structures of the perovskite SrTiO₃ without the use of any structure-directing agents.

Research into complex multicomponent materials is exemplified by the sustainable semiconductor Cu₂ZnSnS₄ (CZTS). Peukert *et al.* (DOI: 10.1039/C5CE00661A) provide an in-depth investigation of the formation and depletion of nanoparticulate CZTS,

advancing the understanding of the conditions required for controlling its crystal structures and compositions. Ryan and Coughlan (DOI: 10.1039/C5CE00497G) probed the early stages of CZTS formation, revealing distinct stages as a result of differing precursor reactivities, and demonstrate a means of controlling particle morphologies *via* the concentration of the amine solvent.

In fact, a series of papers deal with the use of additives for directing and controlling particle formation. Taubert *et al.* (DOI: 10.1039/C4CE02274B) take advantage of the phase behaviour of an amphiphilic block copolymer for the interface-controlled mineralization of calcium phosphate on layered structures rich in poly(acrylic acid) (PAA). Birkedal *et al.* (DOI: 10.1039/C5CE00424A), in turn, used *in situ* X-ray diffraction to study calcite nucleation on the surface of PNIPAM–PAA micelles in a time-resolved manner. Along similar lines, photolithographic polymer films offer great potential as a matrix for controlling the structure of complex CaCO₃ and SrCO₃ hybrid materials, as demonstrated by Kato *et al.* (DOI: 10.1039/C5CE00451A). Wolf *et al.* (DOI: 10.1039/C5CE00441A) contribute to the mechanistic understanding of the formation of such inorganic crystalline films of CaCO₃ from a nanogranular amorphous precursor phase. The interplay of additives can also lead to distinct synergistic effects, which can be exploited for the technically relevant inhibition of calcium carbonate precipitation according to Gebauer *et al.* (DOI: 10.1039/C5CE00452G). Peter *et al.* (DOI: 10.1039/C5CE00676G) used molecular simulations so as to delineate an atomistic picture of a potential mechanism for the oligopeptide-controlled polymorph selection of calcium oxalate. Moreover,

molecular simulation and explicit growth simulations of distinct facets of zinc oxide by Zahn and Milek (DOI: 10.1039/C5CE00358J) show that rough surfaces can establish considerable differences in the binding site and energy required for additive-controlled growth. In another contribution, Zahn *et al.* (DOI: 10.1039/C4CE02078B) applied computer simulations to study the nucleation mechanism of racemic molecular crystals of DL-norleucine.

In their highlight article, Wang and Ni (DOI: 10.1039/C5CE00417A) underpin the potential use of oriented attachment and self-assembly for the development of strategies to control the morphology of nanoparticle assemblies *via* “non-classical crystallization”. Indeed, the analogies between particle-based crystallization and polymerization blur the boundaries between different fields of chemistry, underlining the interdisciplinary aspect of such studies. The elaboration of formation mechanisms is tedious and time-consuming work, and it is often difficult to draw general conclusions that are valid for many systems. Nevertheless, there is no doubt that mechanistic know-how is the basis for rational synthesis design. In this regard, every study in this themed issue contributes a piece to the overall and complex picture of nanoparticle formation, and thus brings us closer to a general understanding of these processes.

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