



Crystal growth of nanomaterials

Cite this: *CrystEngComm*, 2021, 23, Georg Garnweitner,^a Kwangyeol Lee^b and Dongfeng Xue^c 7874

DOI: 10.1039/d1ce90142g

rsc.li/crystengcomm

The field of nanomaterials continues to be highly dynamic, with more and more complex products being synthesized in highly defined forms. For many applications, crystalline materials with tailored properties are desired, necessitating an adjustment of the size or morphology. In particular, demand for the uniformity of nanomaterials is increasing, anisotropic shapes have often been identified as beneficial or even required for a particular application, and the phase composition of a product needs to be tuned for the best performance. In addition, the direct synthesis of nanostructured composites, hybrids or heterostructures has become highly common, due to the strong synergy of combining two or more components at the nanoscale, in particular in the fields of photocatalysis, catalysis, and electrochemistry. Whilst typically such approaches are experimentally facile, the mechanistic complexity strongly increases, hampering a deeper understanding of the underlying mechanisms and the

interaction of the different components. While the interrelation of the nucleation and growth processes determines the outcome of a synthesis, nucleation is hard to study and, due to the usually fast kinetics, difficult to control. Thus, the growth process becomes important, as in principle it offers the possibility to adapt and tailor particle properties, such as the morphology. Whilst it needs to be stated that not for all materials systems and for all types of syntheses can a distinct growth process be realized, beautiful examples have been reported of adapting the morphology of nanocrystals *via* growth processes, adjusting the crystal size distribution, or of tuning the structure and phase ratio in nanocomposite materials.^{1–6} Growth processes under thermodynamic and kinetic control thus promise the facile tailoring of nanocrystal properties. It is, however, crucial to understand the mechanisms and dependence on the process parameters to fully exploit their potential and pave the road towards their application for the rational adaptation of nanomaterials' properties. For many systems, a host of synthesis strategies have been discussed involving growth steps, but the actual growth processes and mechanisms remain poorly understood.

This themed issue provides a collection of reports that provide a specific, albeit not exclusive, focus on growth processes in the synthesis of nanomaterials. It comprises three highlight articles, two communications,

and eight research articles from research groups around the globe.

The highlight article by Görke and Garnweitner (DOI: 10.1039/d1ce00601k) provides a general discussion of the definition and scope of nanomaterials' crystal engineering, and presents a number of select examples to shed light on its different aspects and potentials. Mourdikoudis and Sofer (DOI: 10.1039/d0ce01766c) focus on pnictogen nanostructures in another highlight article, providing an extensive overview with fascinating examples of the highly diverse morphologies that can be obtained *via* bottom-up chemical synthesis routes.

Several articles deal with the growth of metal oxide nanostructures. The communication by Li *et al.* (DOI: 10.1039/d1ce00255d) reports on the graphene-based growth of Co₃O₄ nanoplates with tunable oxygen vacancies that can serve to greatly improve the electrocatalytic performance. The direct synthesis of ultrathin nanosheets of several metal oxides and hydroxides in water-formamide mixtures is reported by Cölfen *et al.* (DOI: 10.1039/d1ce00277e), who investigate the growth process of the nanosheets to reveal that formamide inhibits the growth along the z-direction and thus is the key component in the system for morphological control. Significantly larger well-defined nanocrystals of copper oxide are presented by Xue *et al.* (DOI: 10.1039/d1ce00273b), who prove that the

^a Institute for Particle Technology and Laboratory for Emerging Nanometrology, Technische Universität Braunschweig, Volkmaroder Str. 5, 38104 Braunschweig, Germany.

E-mail: g.garnweitner@tu-braunschweig.de

^b Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul, 02841, Republic of Korea. E-mail: kylee1@korea.ac.kr

^c Multiscale Crystal Materials Research Center, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen, 518055, China. E-mail: df.xue@siaat.ac.cn

temperature is a main parameter in the synthesis for controlling size and morphology, which can furthermore be applied to optimize the performance of the product as anode material in Li-ion batteries. In an aqueous synthesis in the presence of ammonia, Lv and co-workers (DOI: 10.1039/d1ce00663k) obtained hollow spheres of copper oxide, whereby a transformation of CuO nanoflakes to hollow Cu₂O nanospheres occurred. The surface-directed growth of ZnGa₂O₄ and Ga₂O₃ nanofins with a GaN shell *via* a thermal evaporation process is studied by Nikoobakht *et al.* (DOI: 10.1039/d1ce00744k), whereby the authors discover that, in contrast to previous conjectures, the use of a binary system as a starting material is not necessarily required for promoting the Kirkendall effect.

Other studies are directed to chalcogenides. The formation of CZTS nanoparticles under solvothermal conditions is elucidated by Distaso *et al.* (DOI: 10.1039/d0ce01566k), where a slow re-crystallization and growth mechanism is identified to lead to CZTS from initially formed binary sulphides. A substrate-based growth process of MoTe₂ is studied by Cha and co-workers (DOI: 10.1039/d1ce00275a), where the chemical composition of the substrate is revealed to be more relevant than its crystallinity and surface topography for obtaining high-quality, single-phase films.

Two further articles are focused on metal nanomaterials for electrocatalytic applications. Wang *et al.* present

trimetallic PtPdCu nanoframes with high uniformity that are shown to form *via* a Br⁻ and O₂-assisted etching process and possess high activity towards the methanol oxidation reaction. The communication by Sun, Tang *et al.* (DOI: 10.1039/d1ce00796c) is devoted to ultrafine Pt nanonetworks and proves by a combination of theoretical DFT-based modelling and experiments that surface functionalization with cyano groups can strongly enhance the performance of the material for the hydrogen evolution reaction.

In a more fundamental study, Gebauer and co-workers investigate the mineralization of calcium carbonate, employing an advanced ammonia diffusion method (DOI: 10.1039/d1ce00225b). The authors prove the presence of a dense liquid precursor phase even in the absence of additives. Finally, the issue contains a highlight article by Guo, Garcia *et al.* (DOI: 10.1039/d1ce00234a) in the field of molecular crystals. The authors focus on spin crossover crystalline materials, showing numerous examples that demonstrate the high potential of single-crystal-to-single-crystal transformations for tailoring their molecular bistability and, thus, their switchability.

Such examples on the controlled implementation of the crystal growth principles of nanomaterials pave the road towards rational materials design and engineering, which is fundamental to synthesize multiscale systems with

optimized properties for diverse applications in the fields of energy storage, biochemistry, catalysis, and many others. We hope that this issue may stimulate the exchange of concepts and mechanistic insights between the different classes of materials as well as the different synthesis concepts, and especially motivate young researchers for starting more exciting work in the field of nanocrystal growth.

We would like to express our gratitude to the editorial staff of *CrystEngComm*, in particular Paige Boxhall, Dr. Helen Lunn, Dr. Debora Giovanelli and Dr. Michelle Canning, for their fast and efficient coordination of the invitation, reviewing and editing processes, ensuring the successful completion of this themed issue.

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