gross morphology induced by the structure-directing additives. We demonstrate that highly unusual Co$_3$O$_4$ structures such as thin films or micrometer-sized tubular superstructures composed of elongated nanoparticles can be generated based on bio-inspired concepts.

The products of the polymer- or virus-mediated mineralization reactions are analyzed before and after calcination using a range of imaging, spectroscopic and x-ray scattering techniques. With the aim to ultimately establish structure-property relationships, the electrocatalytic activity of the resulting materials is investigated with respect to model reactions such as electrolytic water splitting.

Figure 1. Bio-inspired mineralization of basic cobalt carbonate mediated by the water-soluble polyelectrolyte poly(vinylamine) (a) and tobacco mosaic viruses as biotemplates (b). Scale bars = 1 μm.

Keywords: bio-inspired mineralization, biotemplates, mesostructure, functional materials, small-angle x-ray scattering

MS14-O2 Complex biomimetic self-assembly in simple inorganic precipitation systems

Matthias Kellermeier$^1$

1. Material Physics, BASF SE, D-67056 Ludwigshafen, Germany

email: matthias.kellermeier@basf.com

Biomineralization provides spectacular examples for the concerted organization of inorganic matter into delicate superstructures with extraordinary properties designed for specific functions. Mimicking these processes in vitro is an overarching goal in material science and other areas of research. However, the currently achieved performance of bioinspired man-made materials does often not approach the natural counterpart yet – essentially due to the complexity of the phenomena leading to biominal formation. Therefore, simplified model systems are needed to understand and ultimately control the fundamental mechanisms of self-assembly at various time and length scales.

Silica “biomorphs” are one such model system. They form upon crystallization of alkaline-earth metal carbonates in silica-rich environments at high pH and display structural and morphological features strongly reminiscent of biominals and other living forms – although no organic matter is involved in their formation. This contribution is meant to give an overview on the fascinating world of silica biomorphs and related structures. It is shown that the interplay of simplest components can lead to the spontaneous development of highly complex architectures if conditions are carefully controlled. A number of recent experimental observations shed light on the processes at work and suggest that dynamic reaction coupling drives self-assembly at the nanoscale, while even more peculiar mechanisms seem to govern the evolution of complex shapes at the micrometer level and beyond. Eventually, different approaches to benefit from the structural concept of silica biomorphs are highlighted along with possible implications for material science and early life detection.

References
Keywords: Biomorphs, biomimetic materials, crystallization, silica, carbonate

Crystal aggregation and orientation in carbonate biological hard tissues such as shells and teeth is organic matrix mediated, a structure consisting of membranes (1A, star) and fibrils (1A, arrow). The gel fibril network creates pores where local crystallization environments resemble those formed by extracellular, biological matrices. In previous studies we investigated in single gel systems the effect of agarose and gelatin on calcite nucleation and aggregate formation [1]. Gel was always occluded into the aggregate and imposed a marked effect on crystal co-orientation and aggregate formation. In Mg-free growth environments, either single crystals or radial aggregates with very few subunits formed. Was Mg added to the growth medium, the amount of internal boundaries increased as well as the number of subunits in the aggregate.

In this paper we discuss the effect on calcite nucleation, growth and aggregate formation of MIXED hydrogel systems. A very first attempt to use a mixture of hydrogels was conducted by Simon et al. [2]. In our experiments we use agarose/gelatine mixtures to crystallize CaCO$_3$ using the double-diffusion method. Mineral microstructure and texture is determined with high-resolution EBSD, the occlusion of gels and characteristics of their distribution is visualized with an FE-SEM on microtome polished, etched and critical point dried sample surfaces. In gel/mineral composites grown in 1:1 agarose/gelatin hydrogels (1B), the hydrogel fabric is characterized by thick fibrils, a high variety of pore sizes and numerous walls. Hydrogels in gel/mineral composites grown in 2:1 agarose/gelatin gels (1C) are dense and consist of thick fibrils but also gel membranes (1C, stars and rectangles). When hydrogels with a 1:1 agarose:gelatin ratio are used (1B), calcite grows as hopper crystals bounded by terraced (104) faces. In an agarose:gelatin ratio of 2:1 used (1C), calcite crystals appear elongated along their c-axis and bounded by extremely terraced very rough and curved (104) surfaces that seem to correspond to steep rhombohedra. In both cases, crystals consist of rhombohedral sub-blocks (size < 1 µm) arranged in an approximately equal orientation. Differences in the occluded gel fabric are the consequence of hydrogel strength and crystallization pressure.