Functional Materials

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Complex Structures of “Sand” and “Chalk”

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In recent years, bio-inspired materials have aroused a great deal of interest due to their promising properties and potential relevance for various applications. Thereby, many studies were carried out in order to elucidate the influence of certain organic (macro)molecules and/or supramolecular matrices, as typically found in biomineralization processes, on the crystallization of naturally abundant minerals. By contrast, our current research is dedicated to explore such effects in purely inorganic environments, namely by using dissolved silica as an additive during mineralization of alkaline-earth carbonates. Under suitable conditions, these simple components can assemble into fascinating architectures, termed “silica biomorphs”, which display morphologies and structures very similar to those produced in biomineralization, such as periodically twisted filaments, flat sheets, or worm-like braids (see Figure 1) [1-3]. Moreover, this methodology allows us to prepare elaborate core-shell-shell nanoparticles in a straightforward one-step process, by slightly changing precipitation parameters (Figure 2) [4]. The formed particles were investigated in detail with HR-TEM and micro-EDX, in order to reveal compositional details.

On the other hand, silica-mediated self-organization mechanisms can also be observed in the absence of carbonate, simply by adding soluble metal salt crystals to alkaline silica sols. The resulting “silica gardens” also show stunning structures reminiscent of living forms such as trees or aquatic plants. Recently, we developed an experimental setup by which we could trace the evolution of relevant species in situ during growth of silica gardens prepared with iron- or cobalt salts [5]. Recently, we have extended this approach to study chemical gardens prepared with calcium salts (Figure 3), as the mechanisms occurring in this system are very similar to those underlying Portland cement hydration. Therefore, calcium-based chemical gardens might serve as model system for detailed analysis of the temporal evolution of dissolution and precipitation processes that occur in the inside of the C-S-H membrane. To characterize these processes, we utilized scanning electron microscopy (SEM) in combination with EDX to investigate structural and compositional details of the formed structures as a function of time.

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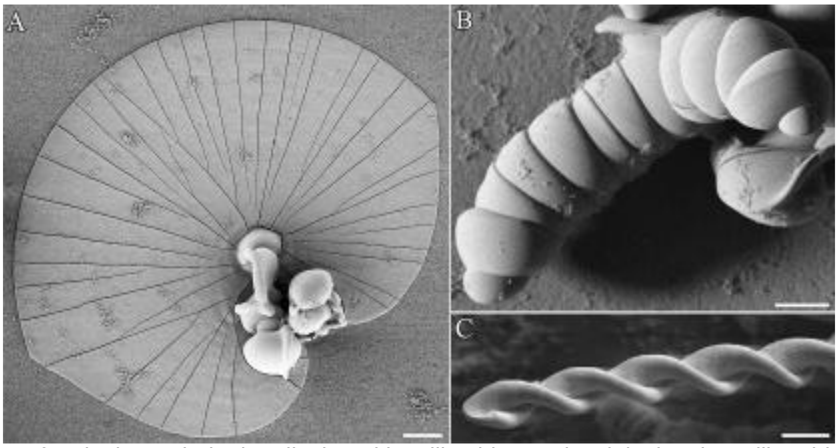

Figure 1. Overview of typical morphologies displayed by silica biomorphs: (A) Flat sheet-like objects, (B) worm-like braids, and (C) complex helical filaments. Scale bar is 20 µm.

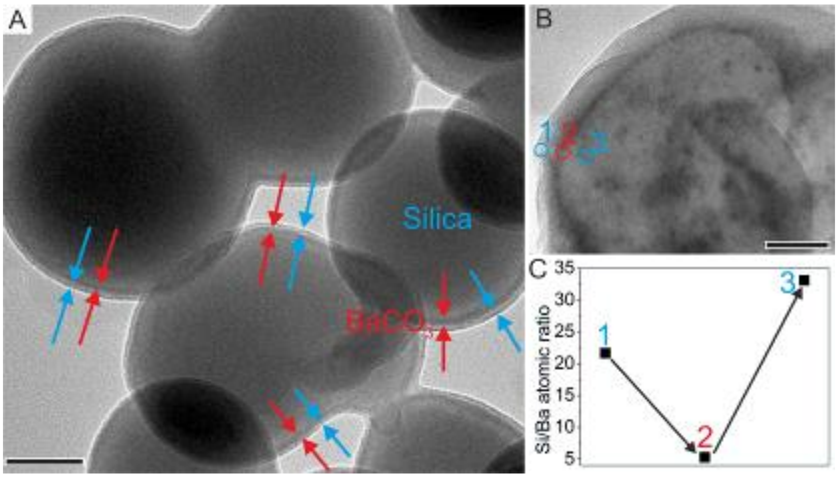

Figure 2. (A-B) Bright field TEM images of core shell-shell particles formed by increasing both, the carbonate and silica supersaturation. Red and blue arrows in (A) mark the interstitial $BaCO_3$ layer and the outer silica skin, respectively (scale bars are 40 nm). (C) Si/Ba atomic ratios calculated from three selected points (as defined by circles in (B)) along an EDX line-scan analysis over the rim of the composite particles. The arrows shall be a guide for the eye.[4]

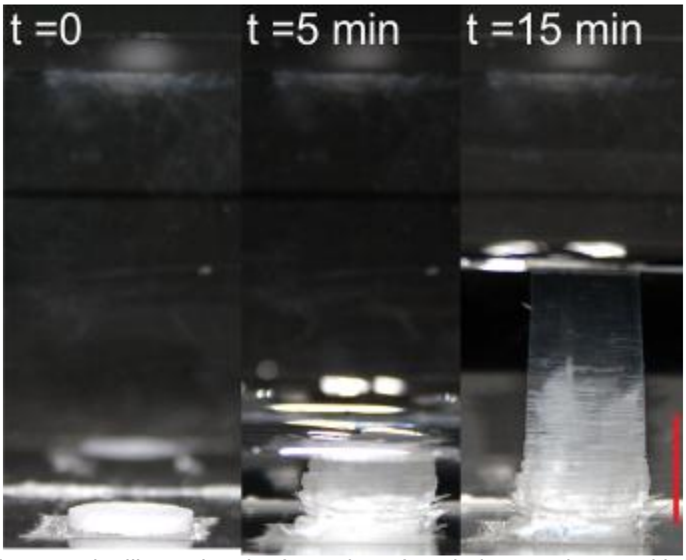

Figure 3. Sequence of photographs illustrating the formation of a tubular membrane with defined dimensions upon addition of diluted silica solution to a tablet of $CaCl_2$. Scalebar is 10 mm.