MS39.O01

Strong stabilization of liquid amorphous calcium carbonate by polymers and proteins

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We have studied the effect of bio-inspired polymers and proteins like ovalbumin, lysozyme and silicatein, which are present in the first stage of egg shell formation or in the formation of siliceous spicules of sponges, on the homogeneous formation of the liquid-amorphous calcium carbonate (LACC) precursor, by a combination of complementary methods like in situ WAXS, light scattering, TEM and cryo-TEM. Lysozyme destabilizes the LACC emulsion, whereas ovalbumin extends the lifetime of the emulsified state. We demonstrate that ovalbumin acts as a stabilizer for a polymer-induced liquid precursor (PILP) process. We propose that the liquid amorphous calcium carbonate is affected by polymers by depletion stabilization and de-emulsification rather than induced by acidic proteins and polymers during a polymer-induced liquid precursor process. Thus, the original PILP coating effect appears to be a result of a de-emulsification process of a stabilized LACC phase. Silicatein-α is responsible for the biomineralization of silica in sponges guides the self-assembly of calcite "spicules" similar to the spicules of the calcareous sponge Sycon. The self-assembled spicules, 10-300 µm in length and 5-10 µm in diameter, are composed of aligned calcite nanocrystals. The spicules are initially amorphous but transform into calcite within months, exhibiting unusual growth along [100]. While natural spicules evidence brittle failure, the synthetic spicules show an elastic response which greatly enhances bending strength. Later stages of nucleation have been studied by "trapping" nuclei from solution by shock-freezing of droplets in liquid ethane (cryo-TEM). This yields snapshots of the structure formation process at given point. In a first step the full determination of the structure of vaterite, one of the common CaCO3 polymorphs, was solved on nanometer-sized crystallites by electron crystallography. These results demonstrate that crystals that are too small for single-crystal X-ray diffraction and too difficult to solve by powder diffraction may nevertheless be amenable to accurate structure determination by electron crystallography.

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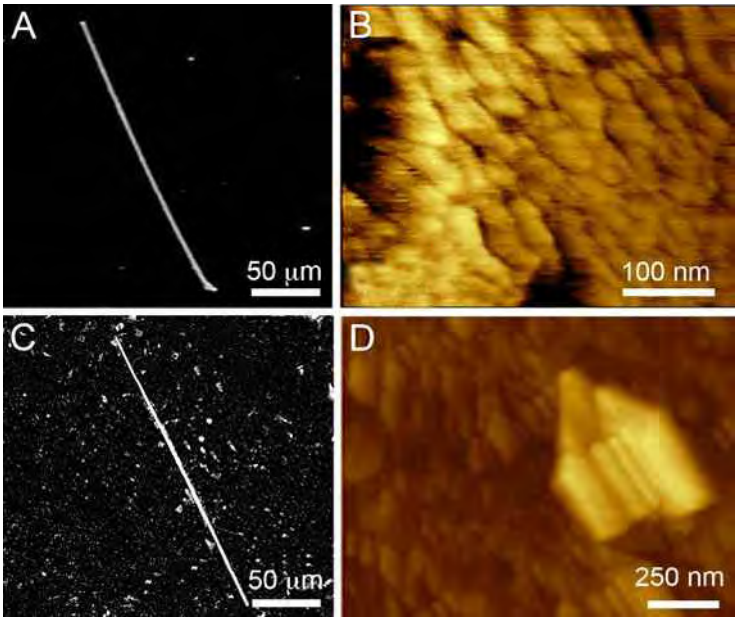

Keywords: Nucleation, Self-Aggregation, Mesocrystal