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Bio-inspired films of crystalline calcium carbonate: 2D patterning by surface-driven liquid-liquid phase separation and hybrid amorphous-to-crystal transformation

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Abstract

Calcareous biominerals, widely found in the living world (shell, skeleton, vision device), present a great variety of forms and biological functions. They, however, gather a number of shared structural characteristics suggesting a common mechanism of formation. In particular, they are in their great majority, composed of a dense assembly of spheroidal crystalline nanoparticles,[1] while having crystalline properties close to those of a single crystal. The formation pathway of these complex materials is not fully established to date, triggering the interest of physico-chemists. As a matter of fact, an increasing amount of evidences suggests that non-classical crystallization involving disordered transient states[2,3] takes place during calcareous biomineralization. Namely, amorphous calcium carbonate has been reported in several aquatic mineralizing species, while the observed space-filling nature of the nanoparticles is suggestive of a mechanism involving a liquid precursor. To assess the relevance of such intermediate states during biomineralization of calcium carbonate, we have developed a model syntheses, involving dense liquid and amorphous phases,[4] further used to produce synthetic calcite crystals. In particular, transiently stabilized amorphous films were produced by exposure of a calcium and polyelectrolyte solution to gaseous carbon dioxide. The resulting films have a sub-micronic thickness and are composed of a dense arrangement of nanoparticles. A newly identified formation mechanism of the films is proposed, which corresponds to the formation of an interfacial 2D pattern by liquid-liquid phase separation, followed by the thickening of the pre-defined 2D pattern by the aggregation of amorphous nanoparticles formed in bulk. The observed peculiar 2D pattern, an assembly of micronic discs, is then used as a morphological marker to explore the crystallization processes triggered under three different conditions: exposure to a high relative humidity, to a high temperature, or during undisturbed aging at the air–solution interface. The investigation of the resulting 2D crystals, in terms of micro- and nanoscale morphologies, allows the determination of the amorphous-to-crystal transformation mechanisms related to each condition. Thus, the crystalline properties resulting from either solid/solid, or hybrid (dissolution/crystallization and solid/solid) transition are investigated and finally compared to those of biogenic crystals. In particular, Bragg ptychography[5] measurements reveal that the crystalline coherence length and the spatial distribution of crystalline defects (tilting and modification of the inter-reticular space) depend on the crystallization conditions. We show that crystals produced by solid-solid transformation in different conditions are not equivalent in terms of crystalline properties, and that they can, in specific conditions, show comparable values of crystalline deformation to the ones of the black lip pearl oyster Pinctada margaritifera.[5]

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