Crystal Hotel : Biomimetic Synthesis of Calcium Carbonate Crystal in Microfludic System

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We report here a novel microfludic approach to enable to investigate the continuous process of heterogeneous nucleation and growth of calcium carbonate. Crystallization occurred in an array of spatially defined 48 individual chambers with tuneable sizes, 50 um to 400 um in diameter and 2.5 um to 150 um in height. Each room provided independent environment facilitating multiple reactions at once.

Initially Ca solutions with or without soluble additives (organic molecules, synthetic polyelectrolytes or proteins) were preoccupied in the total 48 rooms, into where carbonate gas was introduced to initiate precipitation of calcium carbonate. Importantly the gradient level of supersaturation of crystallizing solution in each room was obtained in progressive manner by controlling the flow rate of carbonate vapour. The influence of surface chemistry was also studied by modifying a substrate with self-assembled monolayers with various functional groups.

Examination of the crystals grown directly on a substrate in the array using SEM and raman microscope revealed a number of remarkable features. Each room showed progressive stages of the crystallization due to the gradient level of supersaturation introduced. That is, the room exposed with carbonate gas earlier corresponded to later stage of crystallization, and one occupied later represented earlier stage of crystallizing process. CaCO3 crystallization proceeded significantly more slowly in the smaller room, allowing the mechanism of crystallization to be readily observed. In addition, due to the limited ingredient, the precipitation reaction terminated at an earlier stage than in the bulk solution, easily showing interesting sequences of morphological evolution influenced by the additives with time, which is extremely difficult to capture in bulk crystallization system.

This approach could provide a unique opportunity to study heterogeneous nucleation and crystal growth on directly on desired substrate in environments where the volume and reservoir was restricted. This microfludic design also overcame typical nano/micro reactor issues, such as surfactant contamination and easy solution evaporation.

The results are significant for biomineralization processes, where mineral formation occurs both within compartments and in association with organic matrices, showing that the environment in which a crystal forms can have a significant effect not only on its morphology and orientation but also on the rate of crystallization.