Crystallization of Calcite and Vaterite in Hydrogel-Based Diffusion System

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Biomineralization is a biological process that generates inorganic materials and requires precise control.[1-3] It is delicately controlled in biological systems over long periods of time through slow diffusion and regulated mass transfer, resulting in the formation of intricate structures. Hydrogels have been widely utilized to mimic the microenvironment of biological systems due to their biocompatibility and three-dimensional organic network structure.[4,5] The polymer network of hydrogels significantly restricts the diffusion of substances.[5,6] Therefore, hydrogels are suitable for mimicking the slow and controlled ion transport in biomineralization.[7-9] In this study, calcium carbonate was crystallized within a hydrogel matrix using a cross-diffusion system. Bicarbonate ions and hydroxide ions diffused orthogonally into the agarose hydrogel containing calcium ions. Using this system, the effects of ion flux and pH on calcium carbonate crystallization can be investigated. The regulated ion flux and changes in pH due to the influx of hydroxide ions created a specific microenvironment for the crystallization. As a result, not only calcites in various morphologies but also vaterite phases were formed in a specific position of the hydrogels. Vaterite is metastable, making it rarely found in nature and generally difficult to synthesize. In this system, vaterite is synthesized by controlling the ion flux. Selected area electron diffraction (SAED) analysis confirmed that the crystal phases formed in this system correspond to calcite and vaterite. X-ray diffraction (XRD) analysis revealed that the relative distributions of calcite and vaterite varied at different locations within the hydrogel. This indicates that crystallization can be spatiotemporally controlled by differences in ion flux. This study demonstrates that crystal phase, morphology, and size can be regulated by controlling ion diffusion rates within hydrogels. Furthermore, it provides new insights into crystallization mechanisms under diffusion-limited conditions.

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