

탄산칼슘 결정형태에서 PAA와 온도의 효과

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Effects of PAA additive and temperature on morphology of calcium carbonate particles

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1. Introduction

The controlled synthesis of inorganic materials with specific size and morphology is an important aspect in the development of new materials in many fields such as advanced materials, catalysis, medicine, electronics, ceramics, pigments, cosmetics, etc. Compared with the size control, the morphology control is more demanding to achieve by means of classical procedures of colloid chemistry. Biological systems, however, use biomacromolecules as nucleators, cooperative modifiers, and matrixes or molds to exert exquisite control over the processes of biomineralization, which result in unique inorganic-organic composites (e.g., seashells, bones, teeth, and many others) with various special morphologies and functions. The strategy that organic additives and/or templates are used to control the nucleation, growth, and alignment of inorganic particles has been universally applied for the biomimetic synthesis of inorganic materials with unusual and complex form.

The biomimetic synthesis of calcium carbonate (CaCO_3), one of the most abundant biominerals, has received much attention owing to its wide application in such industrial fields as paper, rubber, plastics, paint, etc. [13]. The application of CaCO_3 particles is determined by a number of strictly defined parameters, such as morphology, structure, size, specific surface area, brightness, oil adsorption, chemical purity, and so on. One of the most important parameters is particle morphology. Therefore, the control of crystal shape and size is fundamental from the viewpoint of technical application. Among more than 60 known biominerals, the two polymorphs of CaCO_3 , calcite and aragonite, are by far the most common, whereas vaterite, a less stable polymorph, is not commonly

formed by organisms. Biomimetic synthesis of CaCO_3 crystals in the presence of organic templates and/or additives has been intensively investigated in recent years. Langmuir monolayers, self-assembled monolayers (SAMs), crystal-imprinted polymer surfaces, and crosslinked gelatin films have been used as templates or matrices for the controlled growth of CaCO_3 crystals. Moreover, a variety of macromolecular additives, including biomacromolecules, a designed peptide, and dendrimers, have exhibited obvious influences on the crystallization of CaCO_3 . The biomimetic synthesis of CaCO_3 thin films has been achieved by using the cooperative effect of organic substrates and soluble polymeric additives. Furthermore, emulsion foams, water-in-oil microemulsions, pseudovesicular double emulsions, and gold colloids have been used as templates to achieve the morphogenesis of CaCO_3 with complex morphologies. Recently, the double-hydrophilic block copolymers (DHBC) have been used as a new additive for the effective control of the morphology of CaCO_3 . These polymers consist of one hydrophilic block designed to interact strongly with the appropriate inorganic minerals and surfaces, and another hydrophilic block that does not interact (or only weakly) with mineral surfaces and mainly promotes solubilization in water. Owing to the separation of the binding and the solvating moieties, these polymers turned out to be extraordinarily effective in crystallization control for various inorganic materials.

In this work, we studied the crystallization of CaCO_3 particles from aqueous solutions in the absence and presence of polyacrylic acid (PAA). The effects of experimental conditions including temperatures and concentration of PAA were investigated and discussed.

2. Experimental

2.1. Preparation

Distilled water was used in this work. The precipitation of CaCO_3 was carried out in glass beakers at different temperature according to the method reported by literatures, respectively. Aqueous solutions of Na_2CO_3 (0.5 M) and of CaCl_2 (0.5 M) were first prepared as stock solutions. In a typical synthesis, a solution of Na_2CO_3 (0.5 M, 1.28 mL) was injected into an aqueous solution of PAA (80 mL, 1.0 g/L) and the pH of the solution was adjusted to a desired pH (e.g., pH 10) by using HCl or NaOH. Then a solution of CaCl_2 (0.5 M, 1.28 mL) was injected quickly into the pH-adjusted solution under vigorous stirring by using a magnetic stirrer. The mixture was stirred for 1 min, and then the solution kept under static conditions for 24 h (unless otherwise

specified) before the product was collected for characterization. In the experiments, the concentration of PAA was varied from 5 to 0.2 g/L, and the temperatures of the solution were kept at 25°C and 80°C, respectively. As reference experiments, the CaCO₃ precipitates were also prepared in the absence of PAA, and all the other conditions kept the same.

2.2. Characterization

The resulting CaCO₃ precipitates were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) patterns.

3. Results and discussion

This may provide new insight into the control of morphologies of calcium carbonate.

The temperatures and concentration of PAA turned out to be important parameters for the control of morphologies of CaCO₃. Various crystal morphologies of calcite, such as plates, rhombohedras, rectangles, ellipsoids, cubes, etc. can be obtained by changing the experimental conditions.

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