

Biomimetic Synthesis of Calcium Carbonate in the Sucrose Solution

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Many studies showed that saccharides or polysaccharides play an important role in the process of biomineralization. In this work, sucrose was used to induce the formation of calcium carbonate. The CaCO_3 crystals were characterized by scanning electron microscope (SEM), Fourier transform infrared spectrograph (FT-IR) and powder X-ray diffractometry (XRD). The results showed vaterite formed easily in the sucrose solution.

Key Words: Sucrose, Calcium carbonate, Biomineralization.

INTRODUCTION

In recent years, the polysaccharide has been found in the process of biomineralization and play an important role. It can change characteristics of nano-structured materials, control the nucleation and growth of inorganic minerals, manipulate the growth of nano-materials in the biomineralization¹⁻³. Mann and Perry⁴ found that organic phase exist in plant silicified trichome (which was confirmed to be nano- SiO_2 later) and its important composition was polysaccharide. Iler⁵ reported that tabasheer contained polysaccharide and aggregated into clusters by the 10 nm-sized SiO_2 particles.

Saccharides are one of important polymers widely presenting in living organisms. Saccharide was also used as organic matrix to biomimetic crystallization of calcium carbonate. A novel aragonite (CaCO_3)⁶ was synthesized with specific morphology by β -cyclodextrin. Glucan⁷ was used as a template to control synthesis of aragonite calcium carbonate.

Polysaccharides or saccharides are formed by natural macromolecule, play an important role in the life system⁸. Using polysaccharides or saccharides as a substrate to study the mechanism of biomineralization make the experimental system closer to the biological system with important theoretical value, but also have a major guiding significance to synthesis biomimetic materials.

EXPERIMENTAL

The anhydrous calcium chloride, sodium bicarbonate and sucrose were analytically pure. All solutions were prepared with doubly deionized water. The size and

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morphology of CaCO_3 precipitates were characterized by using SEM on a DSM 940 A (Carl Zeiss, Jena) microscope. The specimen powders were prepared for SEM analysis by coating each with a thin gold/palladium layer to prevent specimen charging under the electron beam. Calibration of CaCO_3 pellets (in a proportion of 1 % in KBr powder) was performed and recorded with a Nicolet 870 Fourier transform infrared spectrometer between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} . The XRD measurements were made by an MAP18XAHF X-ray diffractometry at a scanning rate of 1 $^\circ/\text{min}$, using a monochromatized CuK_α radiation ($\lambda = 0.154 \text{ nm}$).

Calcium carbonate was prepared according to the previously described methods⁹. There were a small beaker and a large beaker. 0.84 g of sodium bicarbonate was placed at the bottom of a large beaker (250 mL) and 1.11 g of anhydrous calcium chloride was placed at the bottom of a small beaker (100 mL). The small beaker was placed in the large beaker. A series of the sucrose solutions at different concentrations were added to the two beakers. The aqueous solution of the sucrose was not added to the beaker until the solution surface exceeded the inner small beaker wall by 5-6 mm. The sucrose concentration was 0, 5 wt %, 5 wt % (with $2.5 \times 10^{-1} \text{ mol L}^{-1}$ KCl) and 20 wt %, respectively. When a large number of crystals were formed in the reaction vessel, the crystalline calcium carbonate was collected. The obtained crystalline CaCO_3 was filtered through the solution and rinsed with distilled water and anhydrous alcohol at least five times, then centrifuged, dried and collected.

RESULTS AND DISCUSSION

Fig. 1a-d showed typical SEM pictures of CaCO_3 particles precipitated in both the absence and presence of the sucrose. Regular rhombohedral CaCO_3 particles were obtained in the distilled water without the sucrose as shown in Fig. 1a. The sucrose showed a strong influence on the crystal morphology. The particles size 2-4 nm. When the sucrose concentration was 5 wt %, the well-dispersed spherical particles were gained (Fig. 1b). However, spherical particles became smaller with size of ~2 nm and some rhombohedral CaCO_3 particles were obtained after the adding of KCl (Fig. 1c). Surprisingly, when the sucrose concentration was increased to 20 wt % the CaCO_3 particles like catkin (Fig. 1d).

Infrared spectra of CaCO_3 crystals produced in the sucrose of different concentration were shown in Fig. 2. Bands at 876 and 712 cm^{-1} indicated the formation of calcite (Fig. 2a) in the distilled water. While in Fig. 2b-c, simultaneous occurrence of absorption peaks at 876-712 and 744 cm^{-1} indicated the presence of crystalline calcite and vaterite¹⁰. Fig. 2d showed there was only vaterite. The slight discrepancy between experimental and published IR values could be attributed to the required grinding of a CaCO_3 sample with KBr to produce pellets.

The morphology of calcium carbonate particles change obviously with the sucrose concentration increase from the Fig. 2. It was smooth spherical in low concentration while like catkins in high concentration. Although these particles had different morphology, they were most vaterite except formed in the distilled water.

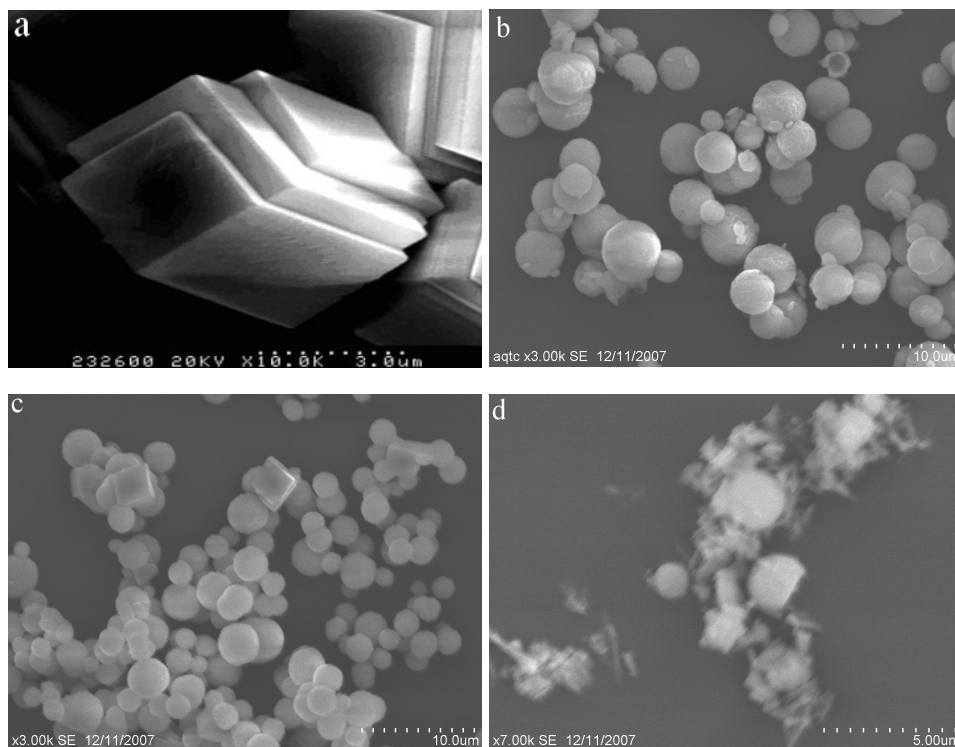


Fig. 1. SEM of CaCO_3 crystal obtained from the sucrose solution sucrose concentration a-d: 0, 5 wt %, 5 wt % (with $2.5 \times 10^{-1} \text{ mol L}^{-1} \text{ KCl}$), 20 wt %

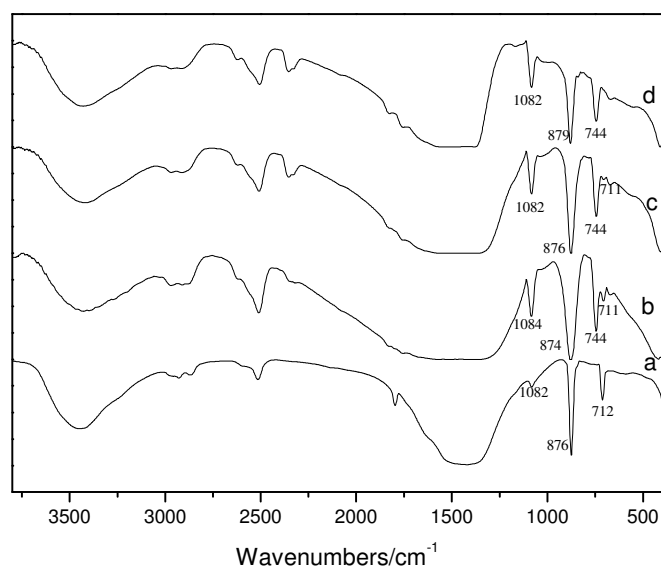


Fig. 2. FT-IR spectra of CaCO_3 crystals obtained from the sucrose solution sucrose

The spherical calcium carbonate particles (Fig. 3b,c) were possibly induced by the sucrose ring molecules. The spherical calcium carbonate particles (Fig. 3d) disappeared when the concentration of sucrose was up to a certain amount. The ionic strength of system increased after adding of KCl. At same time, these ions attracted Ca^{2+} and CO_3^{2-} , respectively. So the gravitation between Ca^{2+} and CO_3^{2-} was reduced which would explain why there were some rhombohedral CaCO_3 particles were obtained after the adding of KCl.

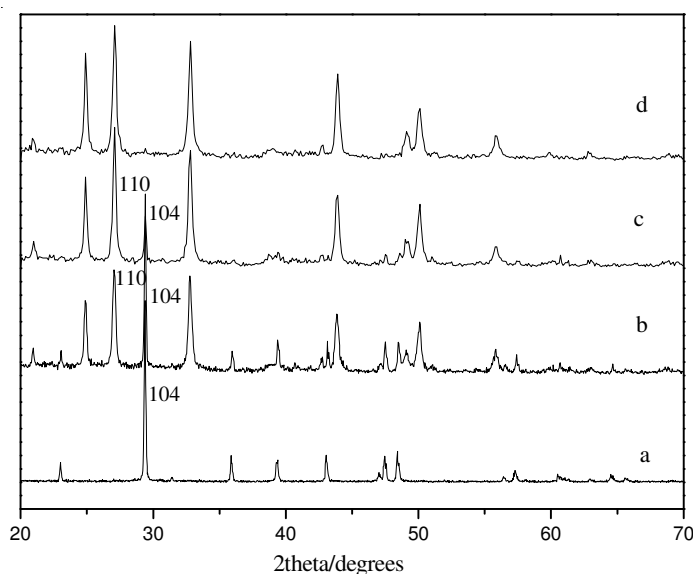


Fig. 3. Patterns of CaCO_3 crystals obtained from the sucrose solution sucrose concentration a-d: 0, 5 wt %, 5 wt % (with $2.5 \times 10^{-1} \text{ mol L}^{-1} \text{ KCl}$), 20 wt %

Assuming that the specimen is a uniform mixture of two components and micro-absorption effects are neglected. For the vaterite-calcite mixture the equation for the calibration line was obtained by linear regression of the experimental data, it can be described by the following relationship (eqn. 1)¹¹:

$$\frac{I_{\text{c}}^{104}}{I_{\text{v}}^{110}} = 7.691 \times \frac{X_{\text{c}}}{X_{\text{v}}} \quad (1)$$

From Fig. 3b,c the intensity ratio $I_{(104)}/I_{(110)}$ were about 2.4, 0.57, respectively, according to eqn. 1, we can calculate that the absolute contents of calcite is 23.5 %, 6.9 %.

Conclusion

The results show that the sucrose can influence precipitation of CaCO_3 from a supersaturated solution. It suggests that the sucrose plays an important role in the regulation of precipitation of calcium salts during the process of biomineralization.

This research may provide new insights into the control of morphologies of CaCO₃ and the controllable synthesis of novel inorganic materials.

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