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Abstract: Calcium carbonate (CaCO3) can show various properties related to its different crystalline phases. For example, the aragonite phase has excellent mechanical strength, whereas the vaterite phase has high water solubility. Therefore, CaCO3 is a useful material for various applications. Wet processes are known to be suitable for preparing metastable CaCO3 polymorphs. Electrolysis has been proposed as a preparation method at ambient conditions. Although several electrolytic approaches have been reported, the effects of the applied current and temperature of the electrolyte on the crystalline phase and morphology of CaCO3 remain unclear. In the present study, we attempted the electrochemical preparation of CaCO3 particles with various electrolysis conditions and discuss the mechanism of CaCO3 particle formation. The crystalline phase and morphology of the CaCO3 precipitates markedly changed depending on the applied current and method of cooling the electrolyte. We assume that these factors were governed by the degree of change in temperature, supersaturation and pH of the electrolyte induced by differences in the electrolysis current.

Control of crystalline phase and morphology of calcium carbonate by electrolysis: effects of current and temperature

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Abstract

Calcium carbonate ($CaCO_3$) can show various properties related to its different crystalline phases and is therefore a useful material for various applications. Wet processes are known to be suitable for preparing metastable $CaCO_3$ polymorphs. Electrolysis has been proposed as a preparation method at ambient conditions. Although several electrolytic approaches have been reported, the effects of the applied current and temperature of the electrolyte on the crystalline phase and morphology of $CaCO_3$ remain unclear. In the present study, we attempted the electrochemical preparation of $CaCO_3$ particles under various electrolysis conditions and discuss the mechanism of $CaCO_3$ particle formation. The crystalline phases and morphologies of the $CaCO_3$ precipitates markedly changed depending on the applied current and method of cooling the electrolyte. We assume that these factors were governed by the degree of change in temperature, supersaturation, and pH of the electrolyte that were induced by differences in the electrolysis current.

Keywords: A: Powders: chemical preparation, E: Biomedical applications, $CaCO_3$

Introduction

Calcium carbonate ($CaCO_3$), an inorganic substance composed of common elements, has attracted considerable attention as a material with a low environmental burden and low risk of resource depletion. $CaCO_3$ exhibits various properties that depend on its crystalline phase; for example, the aragonite phase has excellent mechanical strength owing to its high density [1], whereas the vaterite phase has high water solubility [2]. In the field of biomaterials, vaterite has attracted attention as a novel bioresorbable material with high biological affinity. A nonwoven fabric for bone repair has been prepared from vaterite and poly-L-lactic acid by electrospinning [3] and bioresorbable vaterite microspheres combined with silicate have been developed for bone-forming applications [4].

Wet processes are suitable for preparing $CaCO_3$ with a metastable phase. Crystalline phase control has been attempted by addition of organic substances in aqueous precipitation processes [5,6]. Furthermore, electrolysis has been proposed as a method to prepare $CaCO_3$ polymorphs at ambient conditions. Watanabe et al. applied an alternating current of 10 V/cm to a glass cell containing calcium chloride and sodium

carbonate solutions separated by a membrane and obtained a mixture of calcite and vaterite with a small amount of aragonite [7]. Yamada et al. applied a direct current of 3 to 10 V to a cell containing calcium nitrate and sodium hydrogen carbonate ($NaHCO_3$) solutions separated by a membrane. In this case, addition of sodium nitrate to the electrolyte effectively enhanced the formation of both calcite and vaterite [8]. The effects of the electrolysis conditions on the crystalline phase and morphology of $CaCO_3$ nevertheless remain unclear.

In the present study, we attempted to prepare $CaCO_3$ particles by an electrochemical method by varying the direct electric current and temperature. We discuss the mechanism of $CaCO_3$ formation in detail.

Materials and Methods

Calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$] and hydrochloric acid (HCl) were purchased from Wako Pure Chemical Co., Japan. $NaHCO_3$ and tris(hydroxymethyl)aminomethane (Tris) were purchased from Nacalai Tesque Inc., Japan. The electrolytic cell is shown in Figure 1. The anode and cathode chambers were

filled with 100 mL of 0.5 M $Ca(NO_3)_2$ aqueous solution and an equal volume of 0.5 M $NaHCO_3$ aqueous solution, respectively. Both solutions were buffered at pH 8.5 by Tris and HCl. The reaction compartment between the chambers was filled with 220 mL of Tris buffer at pH 8.5. Platinum foils (Nilaco Co., Japan), 50 mm × 10 mm × 0.1 mm in size, were used for the electrodes. Constant direct current (DC) ranging from 0.2 to 0.6 A was applied by a power supply (ZX-400M, Takasago Ltd., Japan) to the cell for various periods up to 30 min. At some conditions, the temperature of the electrolyte in the cell was controlled by use of cooling water and ice. Precipitates that formed in the reaction chamber were collected by vacuum filtration and dried at 60 °C.

The microstructure of the precipitates was analyzed by powder X-ray diffraction (XRD; MXP3V, Mac Science Co., Japan) with a CuKα X-ray source operating at 40 kV and 30 mA. We also performed scanning electron microscope (SEM; S-3500N, Hitachi Co., Japan) and transmission electron microscope (TEM; H-9000NAR, Hitachi Co., Japan) imaging studies. For SEM observations, the sample surface was coated with Au–Pd alloy by ion sputtering (E-101, Hitachi Co., Japan). A focused ion beam (FIB, FB-2000A, Hitachi Co., Japan) was used to prepare thin films for TEM observations.

Results

For all conditions, white precipitates were observed in the reaction chamber about 2 min after applying the DC electric field. XRD patterns of precipitates obtained at various currents without temperature control or with ice cooling are shown in Figure 2. At 0.2 and 0.4 A without temperature control, calcite, vaterite, and a small amount of aragonite were formed; the amount of calcite was greater than that of the other phases. Conversely, vaterite was the main crystalline phase and a small amount of calcite was formed at 0.4 A with ice cooling. In addition, the amount of aragonite formed at 0.6 A was much greater than in any of the other samples.

SEM images of the precipitates obtained at various currents without temperature control or with ice cooling are shown in Figure 3. The morphologies of the precipitates changed markedly depending on the current value and cooling method, as summarized in Table 1. The shapes of the particles, as shown in Table 1, are schematically illustrated in Fig. 4.

The temperature increased as the current was increased (Figure 5). Even with

ice cooling, at 0.4 A, the temperature increased to 45 °C within 30 min. We assume that the heat generated by the electrolyte at 0.4 A was too high to be maintained at a constant temperature by the ice bath.

Figure 6 shows XRD patterns of precipitates obtained at constant temperature and 0.2 A. The peak intensity of the vaterite increased as the temperature increased and the amount of calcite formed was slightly higher at 30 °C than at other temperatures.

Figure 7 shows SEM images of precipitates obtained at constant temperature and 0.2 A. The morphology of the vaterite particles changed from spherical to hexagonal-shaped, and finally to flower-like, as the temperature was increased (Table 1).

SEM images of the spherical particles prepared at 0.2 A and 25 °C are shown in Figure 8 at low and high magnification. Spherical vateriate was covered with many nanoparticles, of 50 to 100 nm in size.

TEM images and electron diffraction patterns of the surface and inside of particles prepared at 0.4 A with ice cooling are shown in Figure 9. Diffraction rings and diffraction spots from the (200) spacing of vaterite were observed on the surface and

inside of the particles, respectively; thus, the surface and inside of the hexagonal particles comprised vaterite polycrystals and single crystals with c-axis orientation, respectively.

Discussion

$CaCO_3$ was precipitated by simple electrolysis reactions. Ca^{2+} diffuses from the anode to the cathode under a DC electric field, while CO_3^{2-} diffuses in the reverse direction. Limiting ionic conductance of Ca^{2+} (119.0 S·cm^2/mol) is relatively close to that of CO_3^{2-} (138.6 S·cm^2/mol) [9], which means that their ionic mobilities are also similar; therefore, precipitation of $CaCO_3$ would not occur in the anode or cathode chamber, but in the reaction chamber. It is known that about 95 mol% of carbonate ion exists in the form of HCO_3^- at pH 8.5 [10]. $CaCO_3$ with low water solubility is formed by Equation (1) to consume CO_3^{2-}; therefore, the equilibrium in Equation (2) is shifted to the right:

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3; \quad (1)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}. \quad (2)$$

We found that the crystalline phase of electrochemically produced $CaCO_3$ can be controlled by the applied current. The aragonite phase, which is normally difficult to obtain by electrolytic methods, was obtained by increasing the current. Generally, aragonite can be prepared in solutions at high temperatures [11]; therefore, increasing the electrolyte temperature at high current promoted aragonite formation. Monolithic aragonite was not obtained in the present study. Wang et al. demonstrated that monolithic aragonite is difficult to obtain without stirring of the solution, even at high temperature [12]. Monolithic samples are preferable for many practical applications; therefore, the addition of flow apparatus to our reaction chamber or addition of an aragonite stabilizer, such as Mg^{2+}, might be applied to our system to achieve such morphology.

The crystalline phases and morphologies of the precipitates was markedly affected by the method of temperature control, even at the same current (see Figs. 2 and 3), i.e., particles with a hexagonal shape formed at 0.4 A with ice cooling, whereas many flower-like particles formed under all current conditions without temperature control.

Kojima et al. prepared $CaCO_3$ particles with different crystalline phases and

morphologies by heating of $Ca(HCO_3)_2$ solutions at different temperatures and pH, and precisely investigated the mechanism of $CaCO_3$ formation [13]. They showed that the morphology of the vaterite changed from hexagonal to flower-like as the pH decreased. In the present study, the pH of the electrolyte tended to decrease when temperature was uncontrolled (i.e., pH 8.4 at 0.2 A and 30 °C after 30 min, compared with pH 7.9 at 0.2 A without temperature control), in agreement with the above study. Therefore, decreasing pH promotes the formation of flower-like particles.

When the temperature of the electrolyte was maintained constant, the morphology of the vaterite changed from hexagonal to flower-like as the temperature was increased (see Fig. 7). The solubility of $CaCO_3$ decreases as temperature increases [14]; therefore, an increase in the degree of supersaturation with respect to $CaCO_3$ at high temperature promoted the formation of flower-like particles. We note that the morphology of the present particles was governed not only by pH, but also by the degree of supersaturation.

A greater amount of calcite was formed without temperature control than with ice cooling, even at the same current of 0.4 A (see Fig. 2). When the temperature was set to

0.2 A, the amount of calcite was slightly greater at 30 °C than at other temperatures (see Fig. 6). Kojima et al. demonstrated that a single phase of calcite was formed at 30 °C [13]; therefore, we assume that the electrolyte temperature was maintained at approximately 30 °C for a longer time for the former than the latter, giving rise to a greater amount of calcite.

Spherical and hexagonal vaterite were observed at low and high temperatures, respectively (see Figs. 8 and 9). Their formation mechanism is schematically illustrated in Fig. 10. At low temperatures, small nuclei formed: their growth was suppressed owing to the low degree of supersaturation, but nucleation was enhanced by ion diffusion from the anodic and cathodic chambers and the subsequent increase in the degree of supersaturation. Small crystallites aggregated to form spherical particles, as shown in Fig. 8. Conversely, at high temperatures, the formed nuclei vigorously grew into hexagonal particles, owing to the degree of high supersaturation, and then secondary nucleation occurred by ion diffusion from the chambers.

Vaterite single crystals with a similar morphology to that of our particles in Fig. 9 were reported by Zhan et al. [15]. They investigated the formation process of vaterite

prepared by heating of an aqueous mixture of calcium nitrate, gelatin, and urea at 100 °C. Hexagonal crystals covered with nanoparticles formed at 6 h, which transformed to single crystals with clear facets after 1 day. They speculated that the high concentration of gelatin (10 mass%) played an important role in oriented aggregation growth. In the present study, the organic Tris concentration in the electrolyte was only 50 mM; therefore, it would have a small influence on the crystal growth. The formation of $CaCO_3$ mesocrystals in a DC electric field has also been reported [16]; therefore, oriented aggregation growth of vaterite in the present study would be induced by the applied electric field.

We expect that vaterite particles with different morphologies will have applications as bioresorbable drug delivery carriers with desirable release profiles, because the surface area differs between single crystals and polycrystals.

Conclusions

It was found that $CaCO_3$ particles with different crystalline phases and morphologies can be electrochemically fabricated by changing the applied direct current and

electrolyte temperature. In particular, the aragonite phase, which is normally difficult to obtain by electrolytic methods, was observed at high current. Knowledge from the present study can provide a fundamental approach to designing $CaCO_3$ with desired mechanical and biological properties by electrochemical processing.

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Table caption

Table 1 Morphology of the precipitates prepared by various conditions

Figure captions

Figure 1 Appearance of electrolytic cell.

Figure 2 X-ray diffraction patterns of precipitates obtained at various currents without temperature control and with ice cooling.

Figure 3 Scanning electron micrograph of precipitates obtained at various currents without temperature control and with ice cooling.

Figure 4 Schematic illustration of shapes of precipitates formed under different electrolytic conditions.

Figure 5 Changes in temperature of the electrolyte.

Figure 6 X-ray diffraction patterns of precipitates obtained at various constant temperatures and 0.2 A.

Figure 7 Scanning electron micrographs of precipitates obtained at various constant temperatures and 0.2 A.

Figure 8 Scanning electron micrographs of spherical particles prepared at 0.2 A and 25 °C at low and high magnifications.

Figure 9 Transmission electron micrographs and electron diffraction patterns of the surface and inside of particles prepared at 0.4 A with ice cooling.

Figure 10 Schematic illustration of the formation mechanism of vaterite particles with different morphologies.

Table1
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Table 1 Morphology of the precipitates prepared by various conditions

Current / A	Temperature control	Morphology				
		Spherical	Rhombohedral	Hexagonal	Flower-like	Rod-like
0.2	No	Yes	Yes	No	Yes	No
0.4	No	Yes	Yes	No	Yes	Yes
0.4	Ice cooling	Yes	No	Yes	No	Yes
0.6	No	No	No	No	Yes	Yes

Figure1
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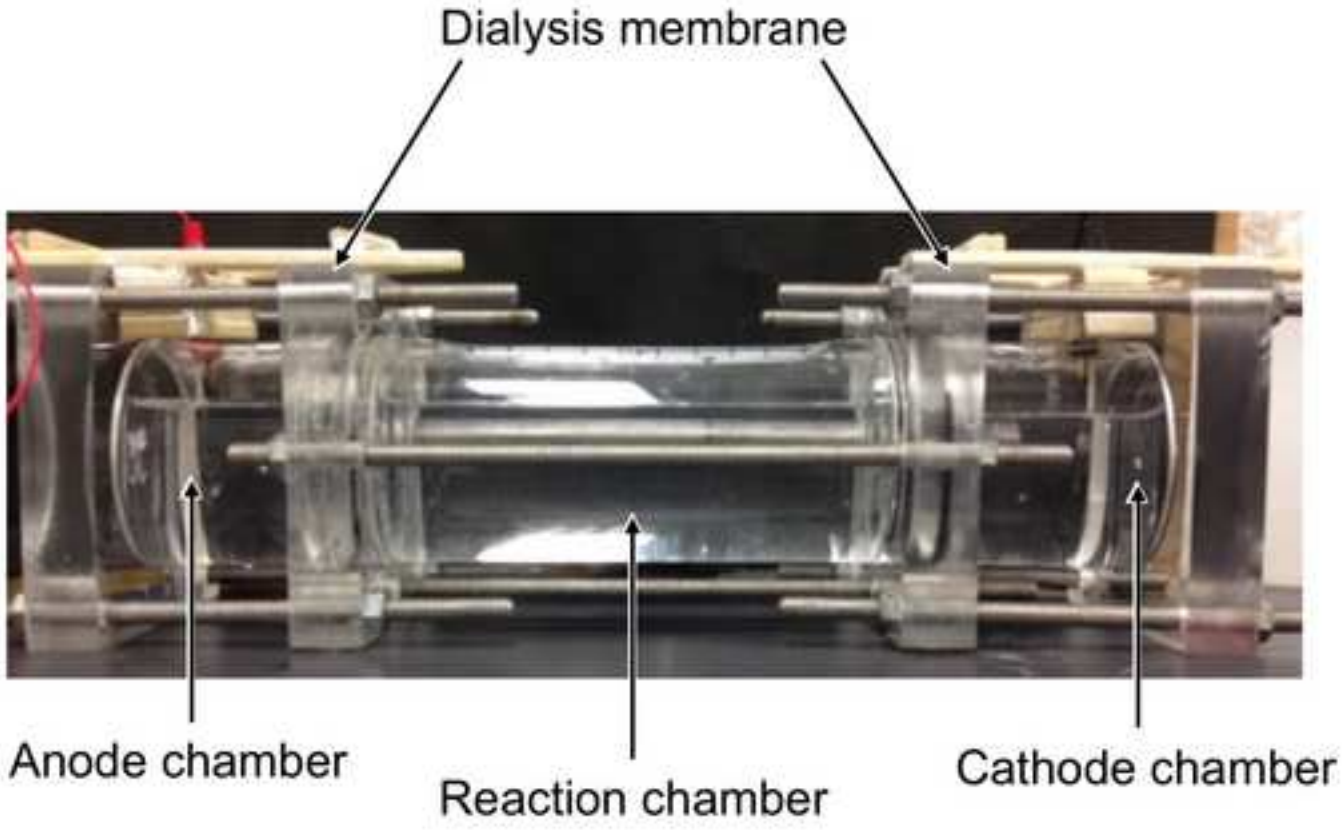

Fig. 1

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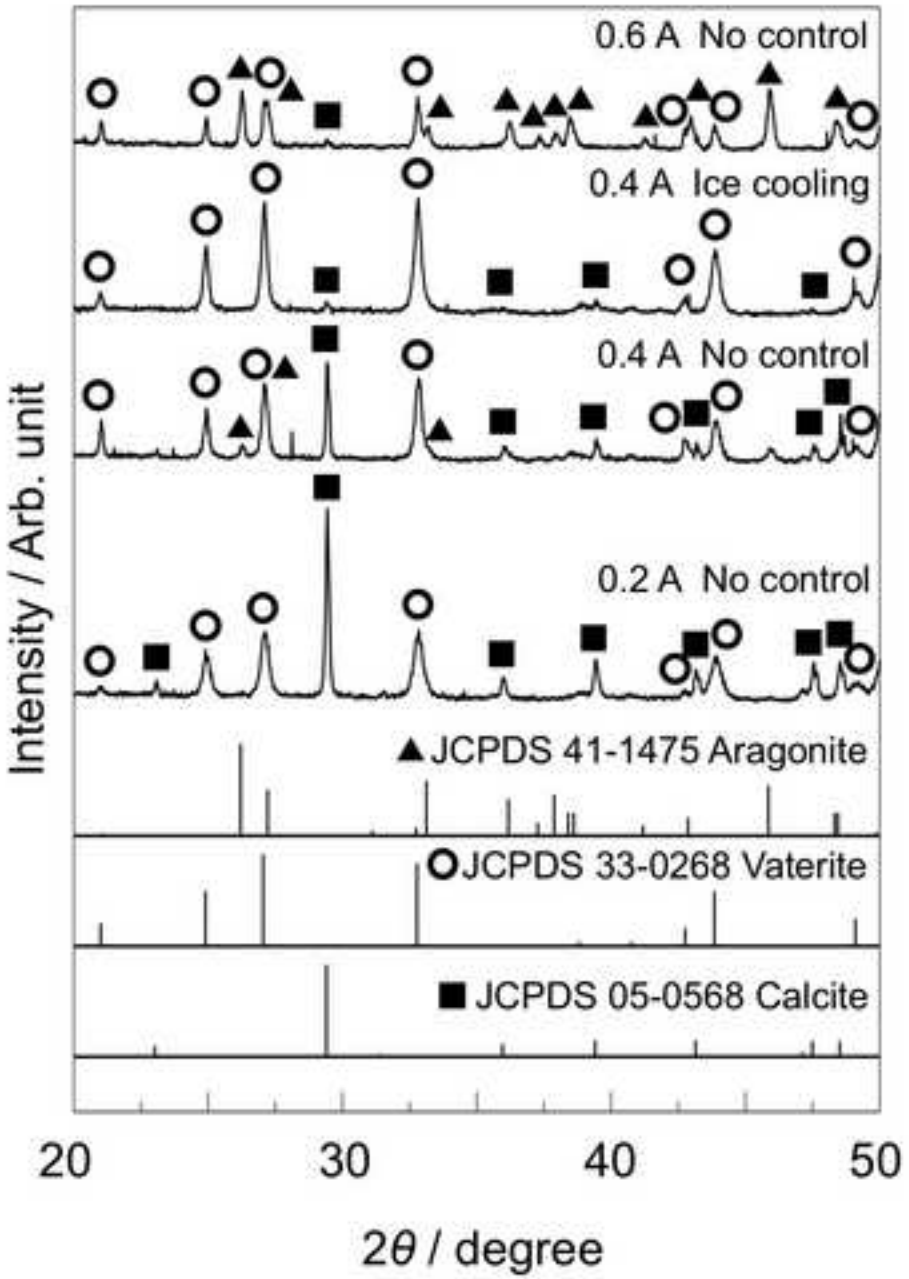

Fig. 2

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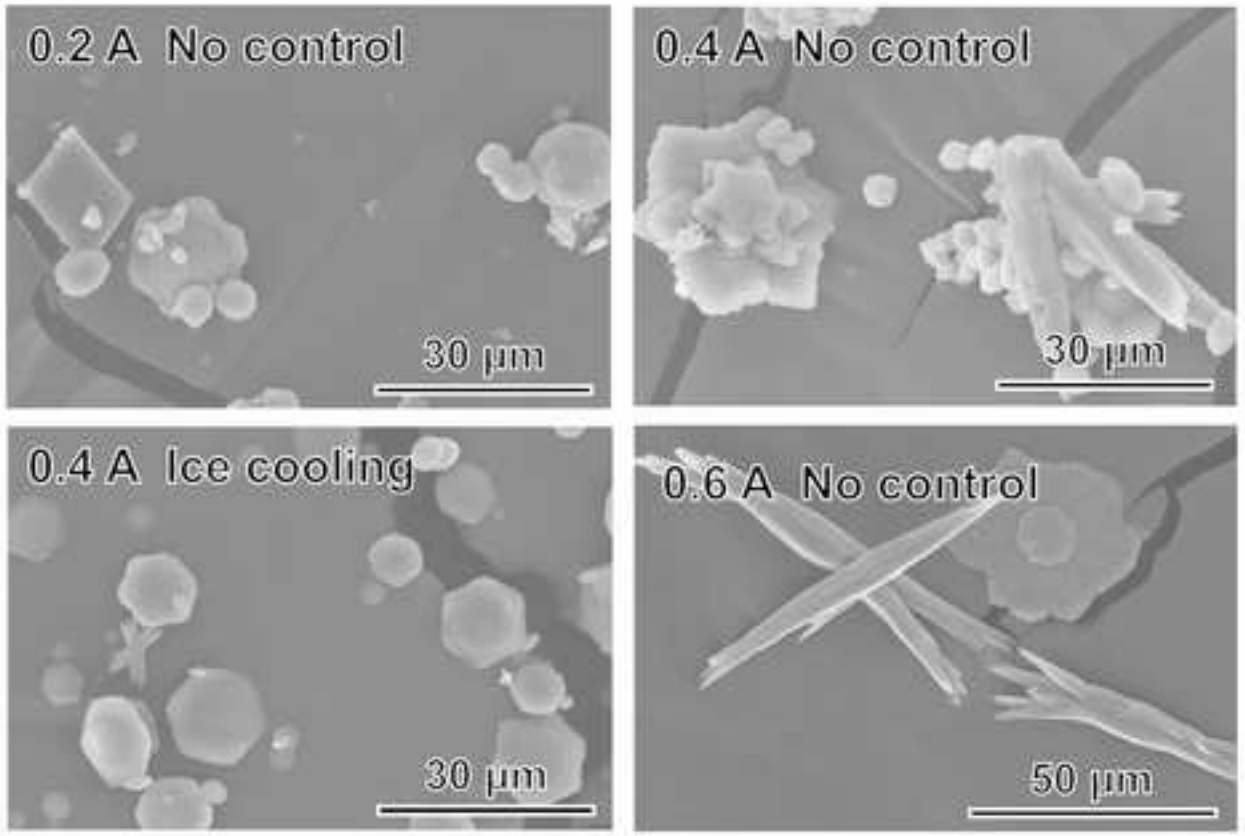

Fig. 3

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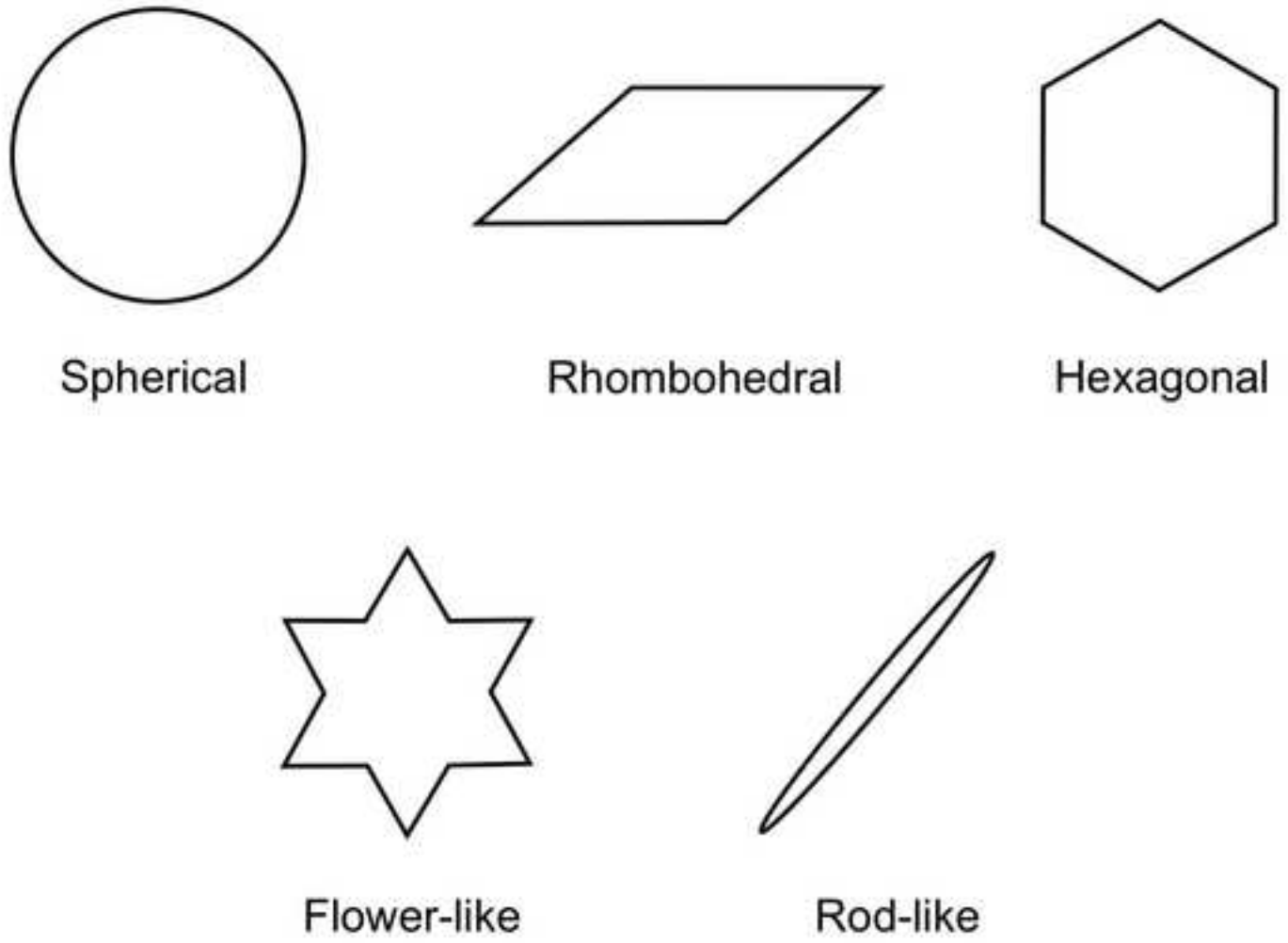

Fig. 4

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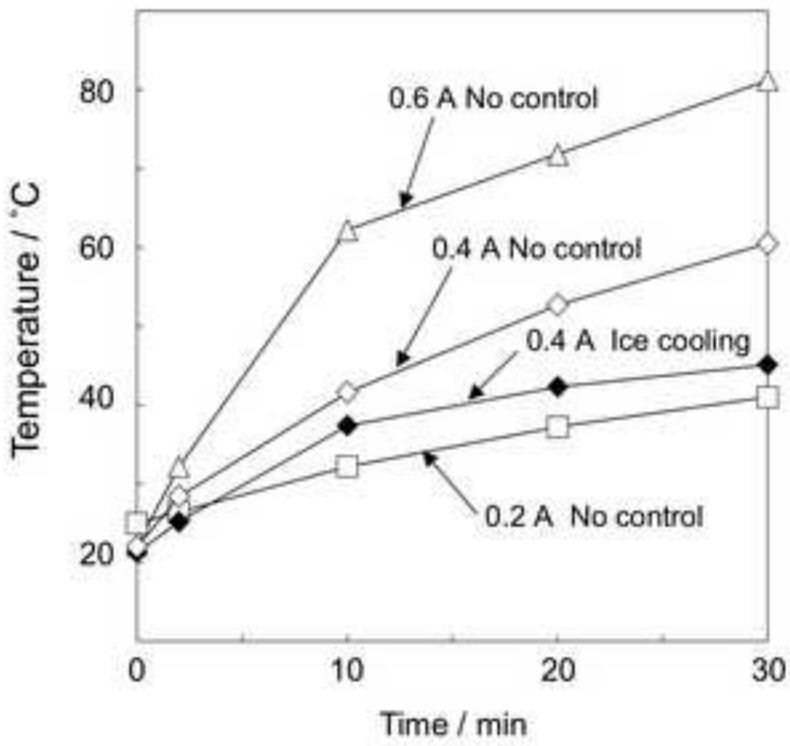

Fig. 5

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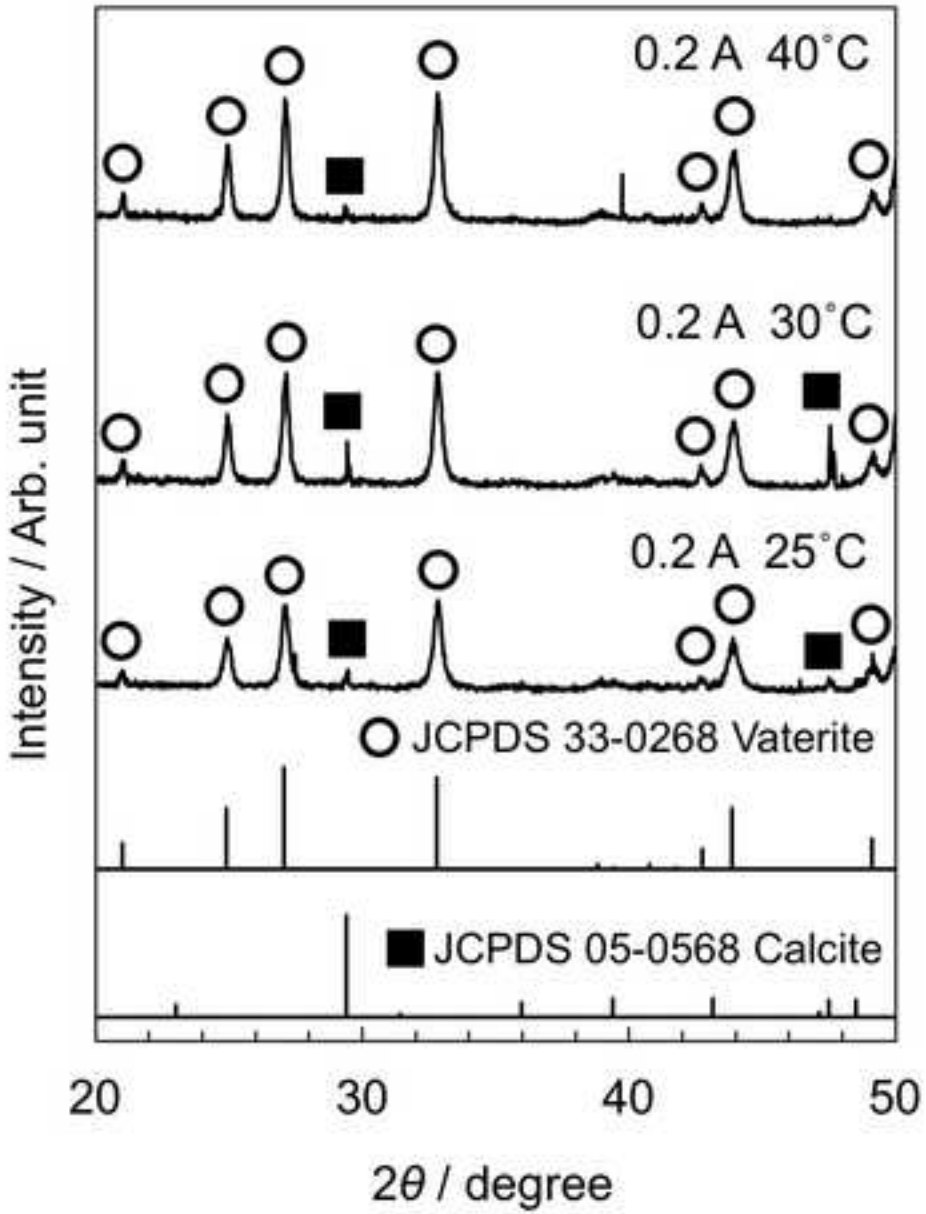

Fig. 6

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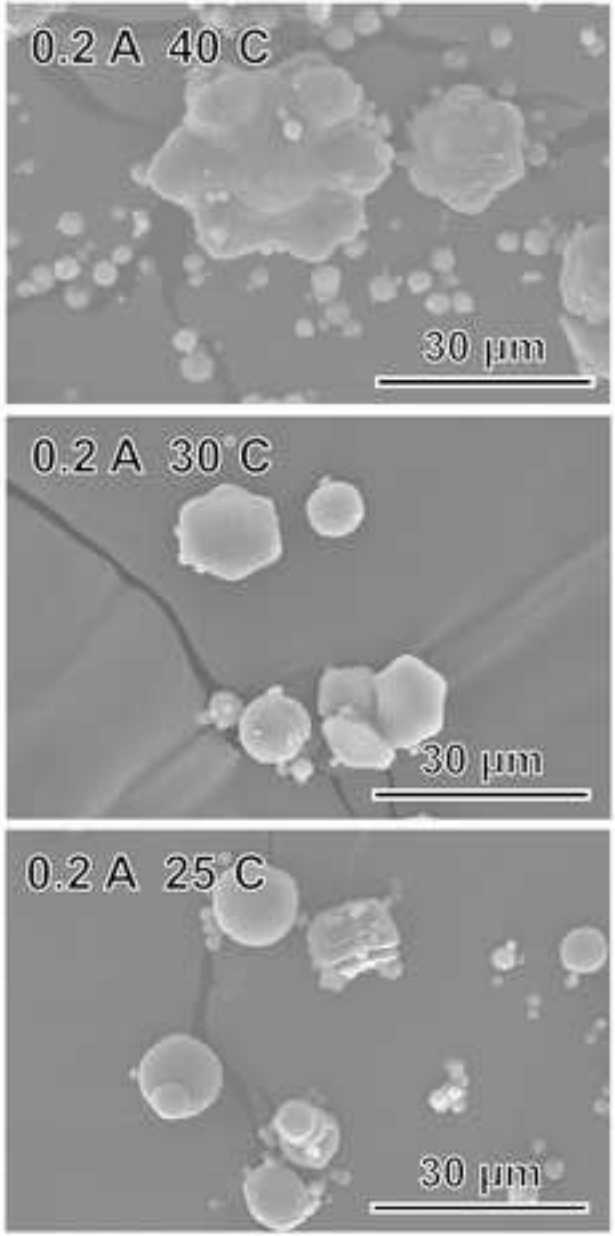

Fig. 7

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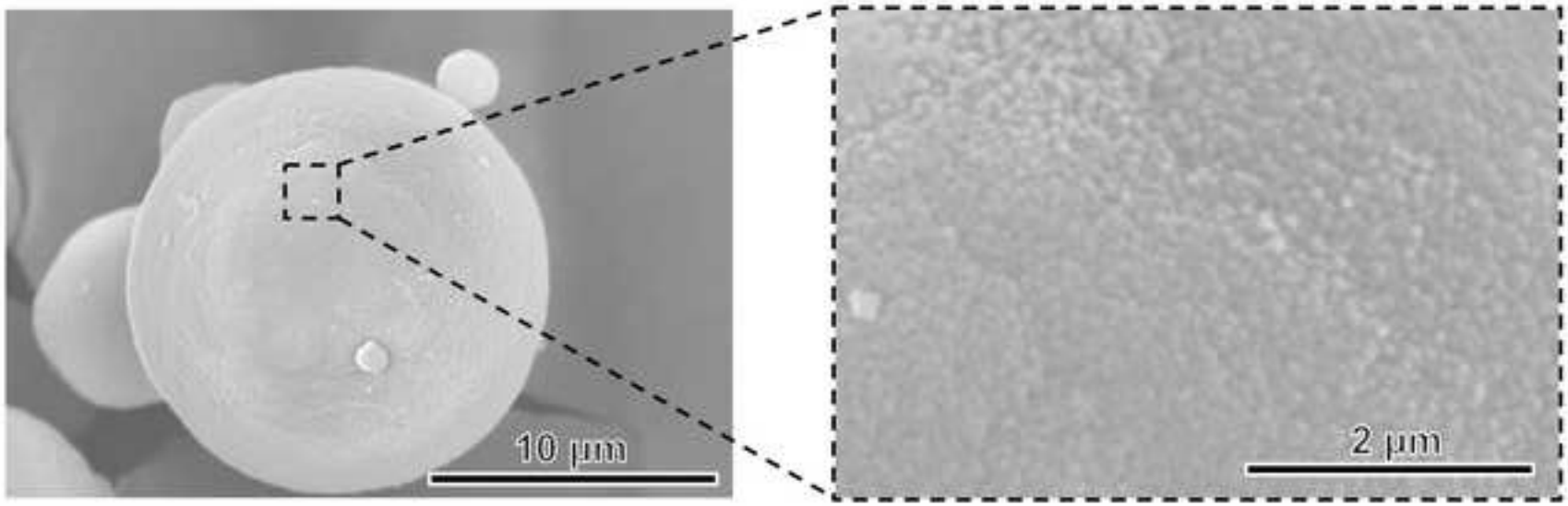

Fig. 8

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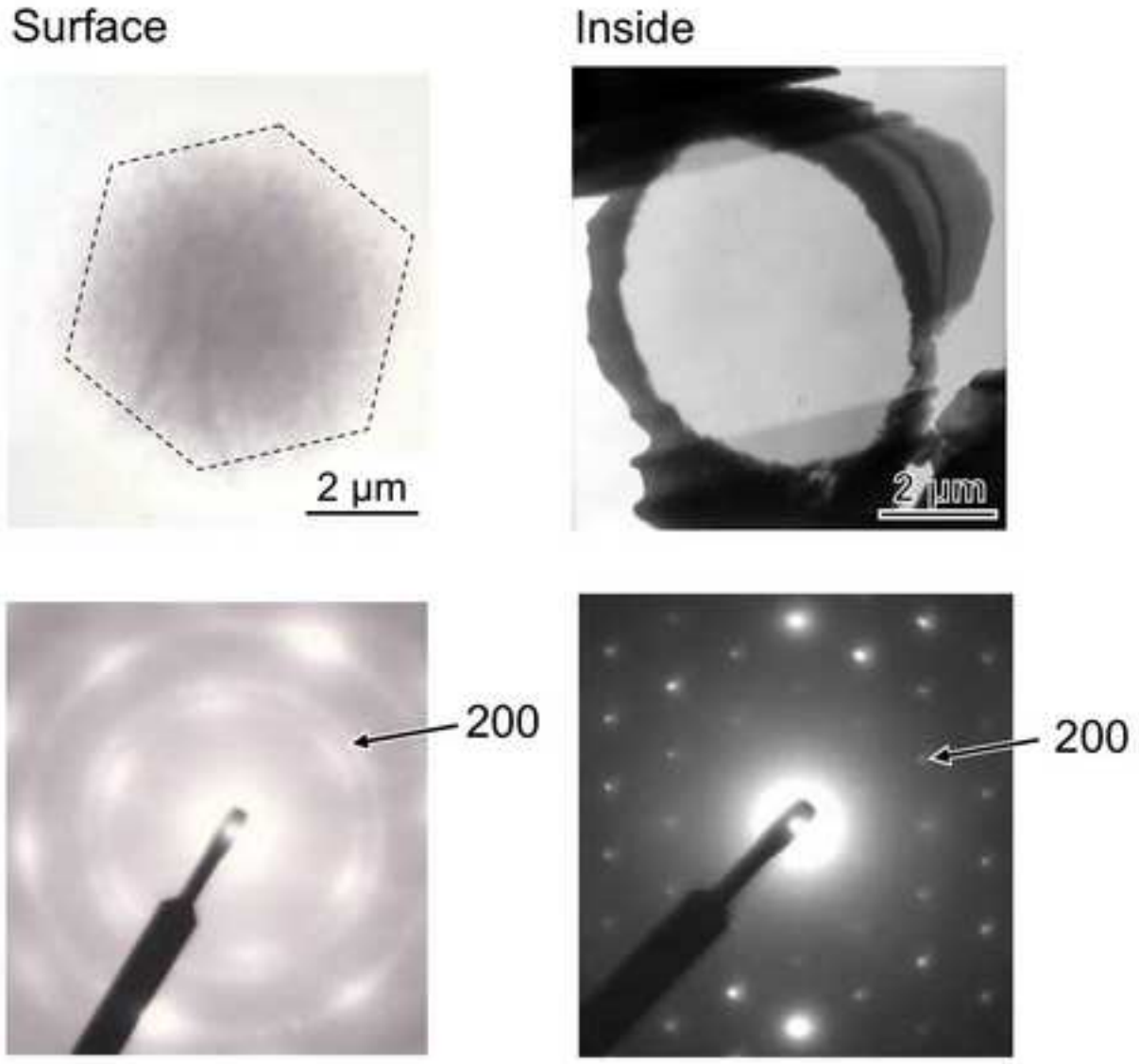

Fig. 9

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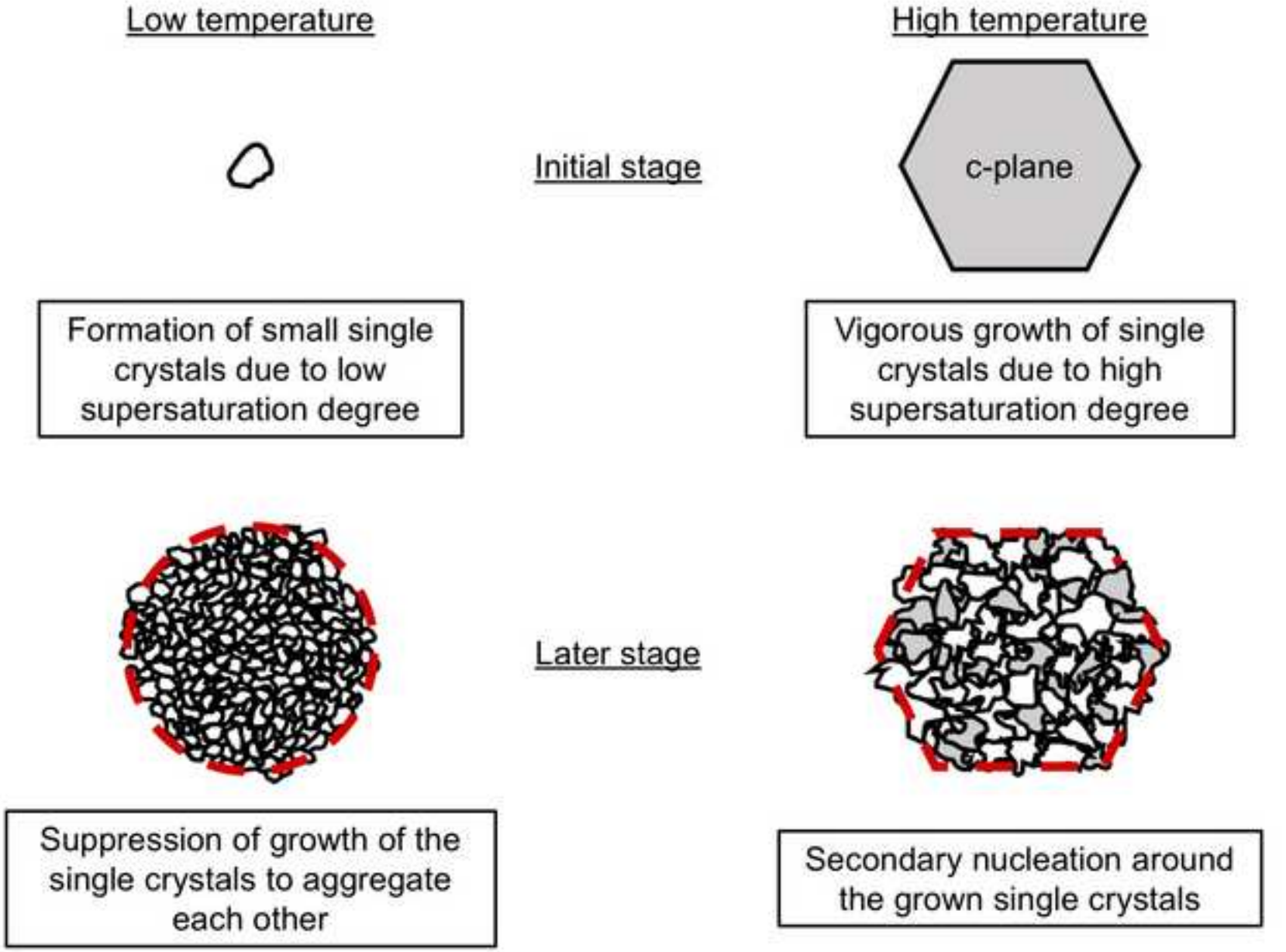

Fig. 10