

Article

Large-Scale Growth of Tubular Aragonite Whiskers through a MgCl₂-Assisted Hydrothermal Process

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Abstract: In this paper, we have developed a facile MgCl₂-assisted hydrothermal synthesis route to grow tubular aragonite whiskers on a large scale. The products have been characterized by powder X-ray diffraction (XRD), optical microscopy, and scanning electronic microscopy (SEM). The results show the as-grown product is pure tubular aragonite crystalline whiskers with a diameter of 5–10 μm and a length of 100–200 μm, respectively. The concentration of Mg²⁺ plays an important role in determining the quality and purity of the products. Furthermore, the method can be extended to fabricate CaSO₄ fibers. The high quality of the product and the mild conditions used mean that the present route has good prospects for the growth of inorganic crystalline whiskers.

Keywords: crystal morphology; whiskers; CaCO₃; growth from solutions

1. Introduction

As an important inorganic material, calcium carbonate (CaCO₃) has been widely used as fillers in paper making, plastics, rubbers and coating due to its low price and richness in the world [1,2]. However, addition of such fillers beyond a certain level sometimes causes some problems such as reduced paper (or plastic, rubber) strength and stiffness. Crystalline whiskers with high aspect ratio,

excellent mechanical properties, and perfect structures represent an ideal class of candidates as reinforcement in composite materials.

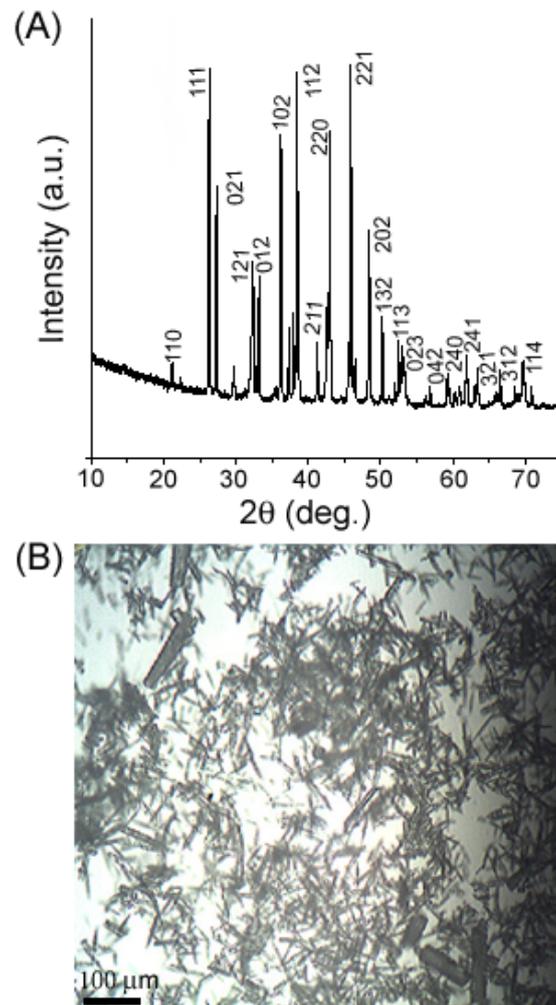
Aragonite, usually occurring in the form of a needle-like crystal, has attracted great interest owing to its great demand for the improvement of mechanical properties of polymer materials. For example, Shang and coworkers found that whisker aragonite performed better than calcite as fillers for polyvinyl alcohol and polypropylene composites [3]. Therefore, many approaches have been developed to synthesize aragonite whiskers. Inspired by the biomineralization processes, scientists have attempted to fabricate CaCO_3 crystals with different morphologies and properties and have investigated the formation mechanisms [4-6]. Water-soluble additives such as metal ions [7,8], anion surfactants [9,10], polymers [11,12], and biomolecules [13] were introduced into the reaction systems to control the shapes of CaCO_3 through specific interactions between the faces of the growing crystals and additives. The carbonation process, in which CO_2 gas is bubbled through aqueous slurry of calcium hydroxide [13,14], is also often used to grow aragonite fibers in terms of environmental preservation and the effective use of mineral resources. However, the shape-control and modification of crystals is difficult, resulting in the limitation of the applicability of the method. Furthermore, granular calcite is usually easily co-produced. Recently, Yu and coworkers [15] have developed an ethanol/water system to realize polymorph discrimination of CaCO_3 in which aragonite nanorods can be obtained by adjusting the ratio of solvents. Hou's group [16] also produced aragonite rods in water/pyridine solution under solvothermal conditions. Unfortunately, these methods require a long time to get the desired product. Developing a facile approach to grow high quality aragonite whiskers under mild conditions still remains a challenge.

Herein, we have developed a convenient hydrothermal route with the assistance of magnesium chloride (MgCl_2) to grow pure aragonite tubular whiskers using urea ($(\text{NH}_2)_2\text{CO}$) and calcium chloride (CaCl_2) as starting materials. The influencing factors such as concentration, time, and Mg^{2+} additive have been investigated. Microscopy images show that the length of whisker is up to several hundred micrometers. Moreover, the method can be extended to prepare CaSO_4 fibers. The high quality of whiskers, environmental benignity and low-temperature used mean the present method is promising in industrial applications.

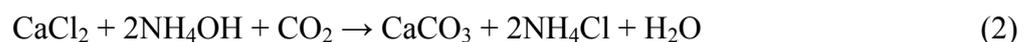
2. Results and Discussion

The phase and morphology of the products have been determined by XRD and optical microscopy and SEM. Figure 1 is the XRD pattern and optical microscopy image of the obtained aragonite whiskers. The XRD pattern shown in Figure 1(A) can be indexed to the orthorhombic phase CaCO_3 with lattice constants $a = 0.496$ nm, $b = 0.797$ nm, $c = 0.574$ nm, consistent with the reported values (JCPDS PDF Card 76-0606). No calcite phase can be detected in the pattern, indicating that pure aragonite CaCO_3 has been produced in the present process. The optical image in Figure 1(B) indicates that the product is composed of a large quantity of tubular aragonite whiskers with a diameter of 5–10 μm . The length of the whiskers is in a range of 100–200 μm .

Figure 1. X-ray diffraction (XRD) pattern (A) and optical microscopy image (B) of the as-grown aragonite whiskers.



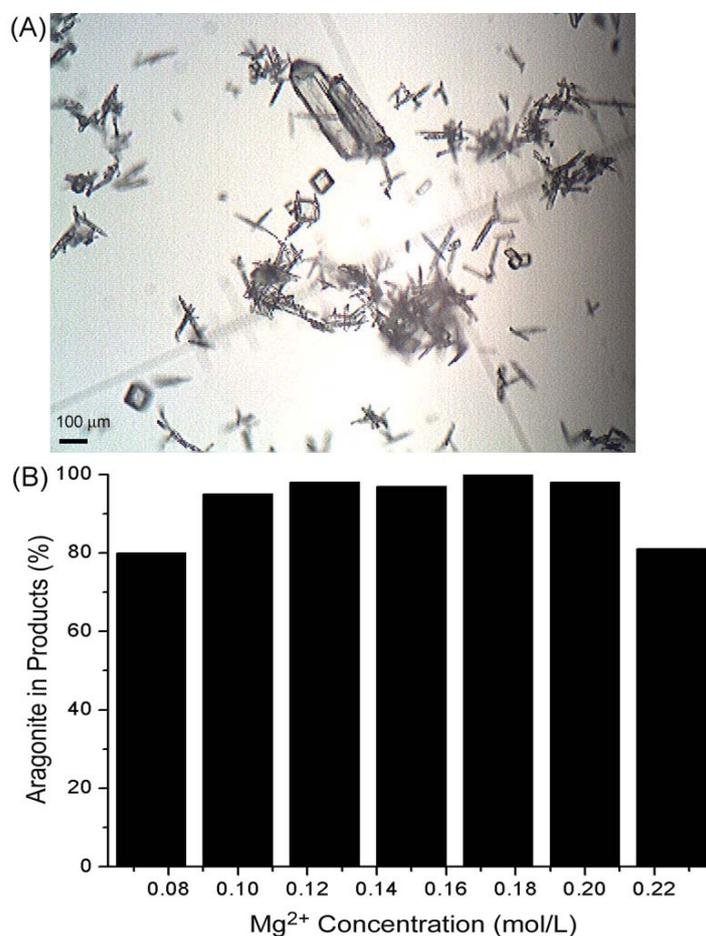
It is known that high precipitation rate facilitates the formation of calcite phase because it has greater entropy than aragonite [17]. Adjusting the nucleation rate of CaCO_3 is essential to achieve pure aragonite crystals. In our system, the presence of appropriate magnesium ions inhibit the nucleation of calcite and thereby reducing carbonate activity below that required for calcite nucleation [18,19]. The main reactions involved in producing aragonite fibers can be expressed as follows:



Similar cases are also found in oceanic conditions containing Mg^{2+} ions, in which metastable aragonite is precipitated first [18]. Kasuga and Ahn's group [14,20] also demonstrated that Mg^{2+} played an important role in producing pure aragonite fibers in the carbonation process. Therefore, the purity of the aragonite can be controlled by changing the Mg^{2+} concentration. If excess Mg^{2+} is introduced, according to reaction (1) and (3), CO_2 releases from reaction 1 will be fast and nucleation favors the formation of calcite. When little Mg^{2+} is used, the ability to control the nucleation rate of CaCO_3 is weak and thus results in the occurrence of calcite. Here, we investigated the influence of the

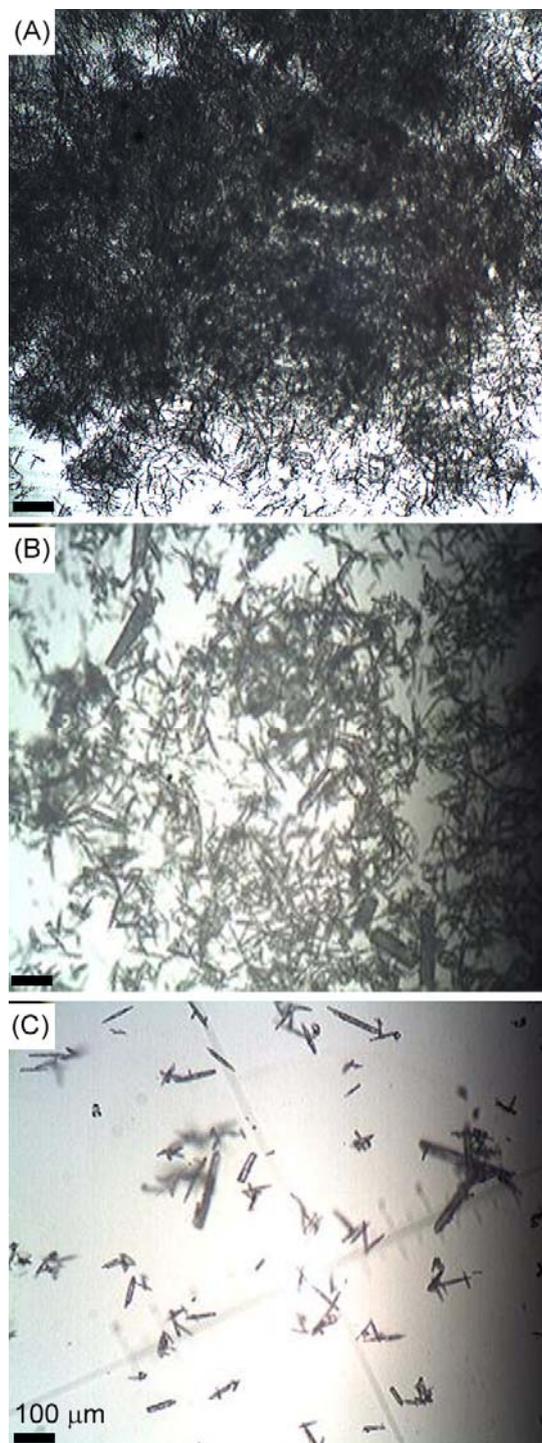
ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ on the formation of aragonite tubular whiskers. It is found that the proper ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ is from 63 to 8. For example, if Ca^{2+} concentration is kept at $0.36 \text{ mol}\cdot\text{L}^{-1}$, MgCl_2 can be introduced in a range of $0.1\sim 0.2 \text{ mol}\cdot\text{L}^{-1}$ and the resulting products are mainly composed of aragonite whiskers (Figure 2B). When $0.075 \text{ mol}\cdot\text{L}^{-1}$ Mg^{2+} ions is used, the optical image (Figure 2A) shows that some calcite crystals with rhombus shape have been entrapped in the product. On the other hand, excess Mg^{2+} (e.g., $>0.2 \text{ mol}\cdot\text{L}^{-1}$) also leads to the increase of calcite in the products (Figure 2B). Of course, detailed studies are necessary to give insights into understanding the role of Mg^{2+} in yielding tubular aragonite whiskers.

Figure 2. (A) Optical image of the product obtained with MgCl_2 concentration of $0.075 \text{ mol}\cdot\text{L}^{-1}$; (B) Variation of aragonite production with Mg^{2+} concentration when the Ca^{2+} is fixed at $0.36 \text{ mol}\cdot\text{L}^{-1}$.



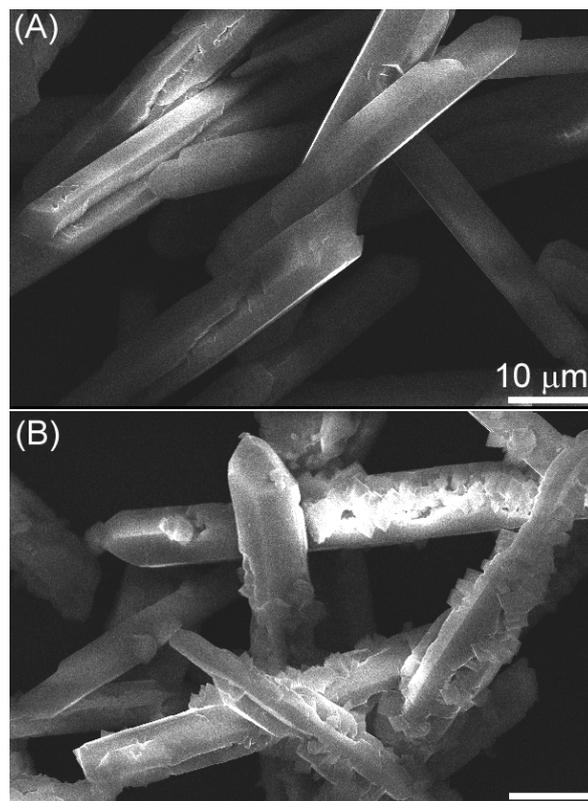
For real applications, the yields of the products in one-pot reaction are also very important. As shown in Figure 3, when CaCl_2 , $(\text{NH}_2)_2\text{CO}$, and MgCl_2 are varied in an appropriate ratio, (*i.e.*, $0.06\sim 1.44 \text{ mol}\cdot\text{L}^{-1}$ for CaCl_2 , $0.18\sim 4.32 \text{ mol}\cdot\text{L}^{-1}$ for $(\text{NH}_2)_2\text{CO}$ and $0.07\sim 0.61 \text{ mol}\cdot\text{L}^{-1}$ for MgCl_2 , respectively), the shape of the obtained aragonite crystals is well retained. It is notable that the yields of the whiskers are reduced as the feedstock concentration decreases. Moreover, high concentrations of feedstocks produce aragonite whiskers in high yields (Figure 3A). When $1.44 \text{ mol}\cdot\text{L}^{-1}$ CaCl_2 is used, the autoclave is full of aragonite whiskers without any liquid. This feature means the present method has good prospects for industrial application.

Figure 3. Optical microscopy images of the aragonite whiskers produced with different concentrations of starting materials (A) $1.44 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$, (B) $0.72 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$, (C) $0.06 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$.



In addition, the investigation of time effect shows that eight hours is appropriate for the formation of whiskers. When the time is less than 8 h, as shown in Figure 4(A), the yield of whisker is decreased on the base of calcium source (e.g., 67.3% for 4 h), indicating that the reaction is incomplete. For longer periods of time (e.g., 10 h), no significant change occurs in the shape of products. Concave cavities (Figure 4B) appear on the surfaces of whiskers, the reason for which remains unclear.

Figure 4. SEM images of the products obtained at different reaction times (A) 4 h (B) 10 h.



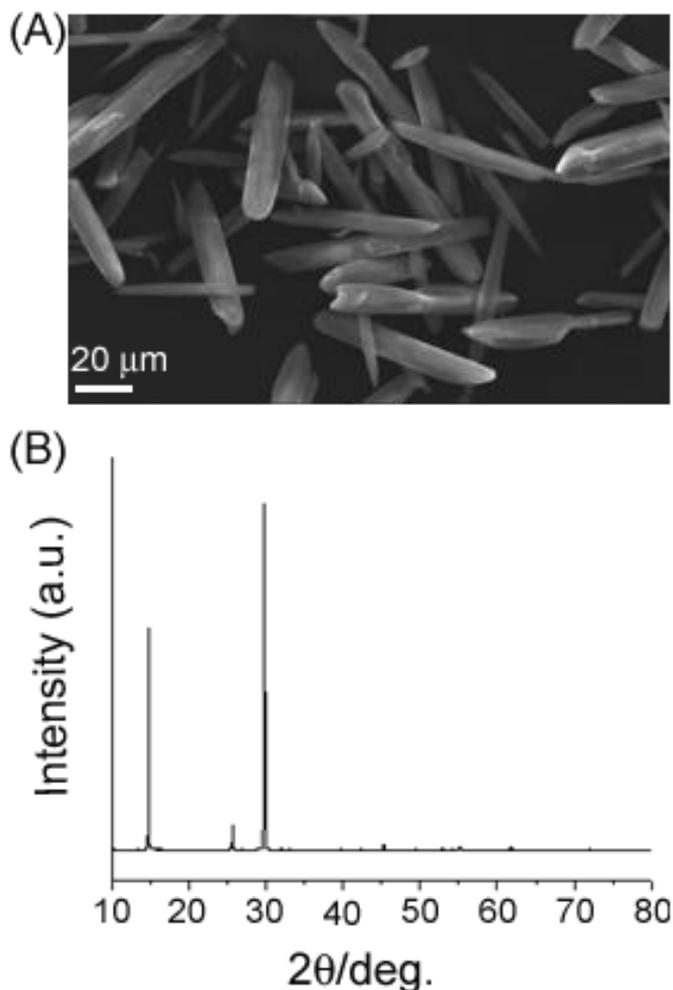
Considering the importance of the whiskers, we try to extend the strategy to grow CaSO_4 fibers by using CaCl_2 , $(\text{NH}_4)_2\text{SO}_4$, and MgCl_2 as starting materials. The SEM image and XRD pattern (Figure 5) shows that spindle-like CaSO_4 crystalline fibers can be successfully obtained using a similar procedure. This result indicates that the present system can be generalized to synthesize other inorganic functional materials and fibers.

3. Experimental Section

In a standard procedure, anhydrous calcium chloride (CaCl_2 , 6.72 g), urea $(\text{NH}_2)_2\text{CO}$, 10.9 g) and magnesium chloride (MgCl_2 , 2 g) were dissolved in 42 mL of distilled water to form a homogenous solution. Then the solution was transferred to a Teflon-lined autoclave with the capacity of 50 mL and maintained at 155 °C for 6–8 h. After the reaction was complete, CaCO_3 whiskers filled the autoclave. The whiskers were washed with distilled water several times and collected for characterization.

The X-ray powder diffraction (XRD) pattern was carried out on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized $\text{Cu } K\alpha$ radiation ($\lambda = 0.1541874$ nm). The morphology observation was performed on a polarizing microscope (POL-280-C, Beijing Maike) and Hitachi S-4800 field-emission scanning electron microscope (FE-SEM, Japan).

Figure.5. SEM image (A) and X-ray powder diffraction (XRD) pattern (B) of CaSO₄ whiskers produced using a similar procedure.



4. Conclusions

In summary, a facile hydrothermal route with the assistance of MgCl₂ has been developed to grow well-defined tubular aragonite whiskers on a large scale. Mg²⁺ plays an important role in determining the purity and quality of the product. Meanwhile, the present route can be extended to prepare CaSO₄ fibers, indicating that the method may be generalized to grow functional oxide materials. Of course, further studies are still necessary to provide insights into unraveling the crystal growth mechanism.

Acknowledgments

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References

1. Dalas, E.; Klepetsanis, P.; Koutsoukos, P.G. The overgrowth of calcium carbonate on poly(vinyl chloride-co-vinyl acetate-co-maleic acid). *Langmuir* **1999**, *15*, 8322-8327.

2. Enomae, T. Application of hollow calcium carbonate particles to papermaking. In *Proceedings of the Fifth Asian Textile Conference*, Kyoto, Japan, 30 September–2 October 1999; Volume 1, pp. 464-467.
3. He, E.G.; Shang, W.Y.; Chen, S.T. Effects of phosphate ion on the growth of aragonite whisker in heterogeneous precipitation from suspension of $\text{Ca}(\text{OH})_2$. *Rare Met. Mater. Eng.* **2000**, *29*, 398-402.
4. Nassif, N.; Gehrke, N.; Pinna, N.; Shirshova, N.; Tauer, K.; Antonietti, M.; Cölfen, H. Synthesis of stable aragonite superstructures by a biomimetic crystallization pathway. *Angew. Chem. Int. Ed.* **2005**, *44*, 6004-6009.
5. Pan, Y.; Zhao, X.; Sheng, Y.; Wang, C.; Deng, Y.; Ma, X.; Ying, Y.; Wang, Z. Biomimetic synthesis of dendrite-shaped aragonite particles with single-crystal feature by polyacrylic acid. *Colloids Surf. A* **2007**, *297*, 198-202.
6. Wang, T.; Leng, B.; Che, R.; Shao, Z. Biomimetic synthesis of multilayered aragonite aggregates using alginate as crystal growth modifier. *Langmuir* **2010**, *26*, 13385-13392.
7. Yu, J.; Zhao, X.; Cheng, B.; Zhang, Q. Controlled synthesis of calcium carbonate in a mixed aqueous solution of PSMA and CTAB. *J. Solid State Chem.* **2005**, *178*, 861-867.
8. Shaw, W.H.R.; Bordeaux, J.J. The decomposition of urea in aqueous media. *J. Am. Chem. Soc.* **1955**, *77*, 4729-4733.
9. Shen, Q.; Wei, H.; Wang, L.; Zhou, Y.; Zhao, Y.; Zhang, Z.; Wang, D.; Xu, G.; Xu, D. Crystallization and aggregation behaviors of calcium carbonate in the presence of poly(vinylpyrrolidone) and sodium dodecyl sulfate. *J. Phys. Chem. B* **2005**, *109*, 18342-18347.
10. Shen, Q.; Wang, L.; Huang, Y.; Sun, J.; Wang, H.; Zhou, Y.; Wang, D. Oriented aggregation and novel phase transformation of vaterite controlled by the synergistic effect of calcium dodecyl sulfate and n-pentanol. *J. Phys. Chem. B* **2006**, *110*, 23148-23153.
11. Kotachi, A.; Miura, T.; Imai, H. Morphological evaluation and film formation with iso-oriented calcite crystals using binary poly(acrylic acid). *Chem. Mater.* **2004**, *16*, 3191-3196.
12. Liu, D.; Yates, M.Z. Formation of rod-shaped calcite crystals by microemulsion-based synthesis. *Langmuir* **2006**, *22*, 5566-5569.
13. Juvekar, V.A.; Sharma, M.M. Absorption of CO_2 in a suspension of lime. *Chem. Eng. Sci.* **1973**, *28*, 825-837.
14. Ahn, J.-W.; Choi, K.-S.; Yoon, S.-H.; Kim, H. Synthesis of aragonite by the carbonation process. *J. Am. Ceram. Soc.* **2004**, *87*, 286-288.
15. Chen, S.-F.; Yu, S.-H.; Jiang, J.; Li, F.; Liu, Y. Polymorph discrimination of CaCO_3 mineral in an ethanol/water solution: Formation of complex vaterite superstructures and aragonite rods. *Chem. Mater.* **2005**, *18*, 115-122.
16. Nan, Z.; Yan, B.; Wang, X.; Guo, R.; Hou, W. Fabrication of calcite aggregates and aragonite rods in a water/pyridine solution. *Cryst. Growth Des.* **2008**, *8*, 4026-4030.
17. Beruto, D.; Giordani, M. Calcite and aragonite formation from aqueous calcium hydrogencarbonate solutions: Effect of induced electromagnetic field on the activity of CaCO_3 nuclei precursors. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 2457-2461.
18. Henderson, P. *Inorganic Geochemistry*; Pergamon Press: Oxford, UK, 1982; pp. 297-353.

19. Gutjahr, A.; Dabringhaus, H.; Lacmann, R. Studies of the growth and dissolution kinetics of the CaCO₃ polymorphs calcite and aragonite II. The influence of divalent cation additives on the growth and dissolution rates. *J. Cryst. Growth* **1996**, *158*, 310-315.
20. Ota, Y.; Inui, S.; Iwashita, T.; Kasuga, T.; Abe, Y. Preparation of aragonite whiskers. *J. Am. Ceram. Soc.* **1995**, *78*, 1983-1984.

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