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Formation of star-shaped calcite crystals with Mg^{2+} inorganic mineralizer without organic template

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Abstract

Star-shaped calcite crystals with $\bar{3}m$ symmetry were obtained in the mixed solvent of ethanol and H_2O (4:1 vol%) using Mg^{2+} as grow mineralizer without any organic template under the solvothermal condition. The crystals branched to the six directions perpendicular to the *c*-axis. In the process, Mg^{2+} takes an important influence on such novel morphology via entering the crystal lattice of calcite to absorb the special plane and change the general growth habit. The aqueous solvent is favorable to form aragonite, while the presence of alcohol promotes the formation of calcite, the thermodynamically stable phase. The products were characterized by the techniques of XRD, SEM, SAED, IR and ICP. The formation process was also primarily studied.

Keywords: Crystal morphology; Growth from solutions; Star-shaped; Calcite; Magnesium ions

1. Introduction

In recent years, one of the important goals of material scientists is to develop ways of tailing the structure of materials with unusual and special morphology [1–3]. The biomimetic synthesis of inorganic materials with complex form has been inspired due to the remarkable range of morphologies exhibited by biominerals. In this process, most notably, calcium carbonate polymorphs of different size and shapes have been intensively investigated due to their importance in geo- and biosciences, as well as numerous important industrial applications as a filler in paints, plastics, rubber, or paper [4–6]. Generally, there are two kinds of additives to fabricate $CaCO_3$: the organic matrix and the inorganic mineralizer. An organism creates the proper organic matrix as a substrate for the nucleation, and inorganic crystals can precipitate onto the matrix due to the interfacial interaction between inorganic and organic materials, which is capable of controlling the shape of resultant inorganic materials. For example, langmuir monolayers [7,8] biomacromolecules [9,10], dendrimer [11,12], double-hydrophilic block copolymers [13,14] and emulsion foams [15] have been widely used as effective templates for the controlled growth of $CaCO_3$.

Although the most intensely examined systems are mainly related to organic templates or additives on the biomimetic synthesis of $CaCO_3$ with various kinds of morphologies, very little is still known about its biomimetic morphology in the presence of inorganic mineralizer. Among the inorganic mineralizers, Mg^{2+} has been attracting much attentions because the skeletons of many organisms is composed of magnesium-bearing calcite and there exist larger quantities of Mg^{2+} ions in seawater, in addition Mg^{2+} is believed to play a critical role in the formation of $CaCO_3$ in the biological environments. Some investigations on the morphological changes in calcite crystals induced by Mg^{2+} were reported before, for examples, Mg^{2+} additive was reported to induce the spherulite core/shell and elongated particle from calcite spherulite morphology [16]. Magnesium calcite crystallization from water–alcohol mixture has been reported, and

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the irregular morphological calcite was obtained [17]. However, no oriented nucleation and growth were observed until most recently, when Aizenberg et al. pioneered the morphology investigation using Mg^{2+} as the growth modifier and carboxylic acid functionalized SAMs as template and tetrahedron-like, prism-like and spindle-like calcite crystals with oriented nucleating planes were obtained [18].

Pure calcium carbonate generally contains two common polymorphs as calcite and aragonite. Calcite is the stable phase and aragonite is thermodynamically less stable. Recently, a template route applying Ca^{2+}-keggin anion colloidal particles produce star-shaped calcite crystals with two 3-fold rotation symmetrical tetrahedral units joined at one vertex but rotated by 60° relative to each other [19]. Star-shaped calcite single crystals with well-defined eight arms were formed by crystallization of $CaCO_3$ in agarose gels [20]. In this work, star-shaped clacite microcrystals having six arms with $\bar{3}m$ symmetry was obtained in mild solvothermal condition with the addition of magnesium ion. To the best of our knowledge, this is the first time to observe the star-shaped morphology of calcite crystals with $\bar{3}m$ symmetry induced by magnesium ions without any organic template.

2. Experimental section

2.1. Preparation of star-shaped calcite microcrystal

Analytical grade solvents and reagents were purchased from Shanghai Chemistry Co. Ltd. The detailed processes of synthesizing star-shaped calcite were following: $CaCl_2$ (3 mmol), urea (3 mmol) and $MgCl_2$ (3 mmol) were dissolved in the 10 ml solvent of ethanol/H_2O (4:1 vol%) in a flask. On stirring to completely dissolve, the mixtures were added to a Teflon-lined autoclave of 15 ml capacity, heated and maintained at 120 °C for 12 h, and then gradually cooled to room temperature. The white powders were carefully collected, washed with distilled water and ethanol for several times respectively and dried in vacuum at 60 °C for 4 h.

2.2. Characterization of the products

The phase and the crystallographic structure of the products were determined by X-ray powder diffraction (XRD) using a Japan Rigaku D/max-rA X-ray diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The scan rate of 0.05°/s was applied to record the patterns in the 2θ range of 10–70°. The morphology and size of as-prepared products were observed by scanning electron microscopy (SEM), performed on an X-650 scanning electron microanalyzer with an accelerating voltage of 25 kV. The selected area electronic diffraction (SAED) patterns were taken on a Hitachi Model H-800 transmission electron microscope with a tungsten filament, using an accelerating voltage of 200 kV. IR spectra were measured on a Bruker Vector-22 FT-IR spectrometer at room temperature. The content of magnesium ions of star-shaped calcite were measured via inductively coupled plasma (ICP) spectroscopy with a Seiko Electronics SPD 1200 A ICP emission analyzer. Distilled HCl solution is used to dissolve the powdered samples.

3. Results and discussion

XRD patterns are used to illuminate the phase of calcium carbonate polymorph. Fig. 1 shows XRD patterns of the as-obtained product, and all peaks can be indexed to hexagonal calcite (JCPDS No. 5-586). IR spectrum (Fig. 2) provides further evidence of pure calcite. Simultaneous occurrence of absorption peaks at 1417, 873 and 712 cm^{-1} indicates the presence of crystalline calcite [21].

Fig. 3 shows SEM images of the novel star-shaped calcite. Fig. 3a and b both exhibit many star-shaped calcites, which range from 10 to 30 μm in size and look like stars with six arms extending radially. Fig. 3c displays a frontal image of star-shaped calcite. The star-shaped calcite crystal possesses $\bar{3}m$ symmetry. Each arm consists of a long central backbone and very sharp secondary branches, which preferentially grow along two definite directions through certain crystallographic regulation rather than randomly ramified growth. Surprisingly and interestingly, the secondary branches, emerged at 60° with respect to the central backbone, are parallel to each other. A magnified image (Fig. 3d) of an individual arm shows many calcite $\{10\bar{1}4\}$ macrosteps, which indicates the single-crystal nature of the star-shaped crystals. From the SAED pattern (inset of Fig. 3c) taken from the tip of an arm, the single crystalline nature can be further proved.

Judging from SEM results, we speculate that the star-shaped calcite crystals probably evolved from the smaller rhombohedra crystals, which can be testified via the contrast experiments of controlling different reaction times. In early stage of the growth process for 0.5 h, small calcite crystals (~10 μm) with a typical rhombohedra morphology consisting of the basal six $\{10\bar{1}4\}$ planes were obtained (Fig. 4a). At the reaction time of about 2 h, the crystals grew to larger size of about 20–30 μm and dents at

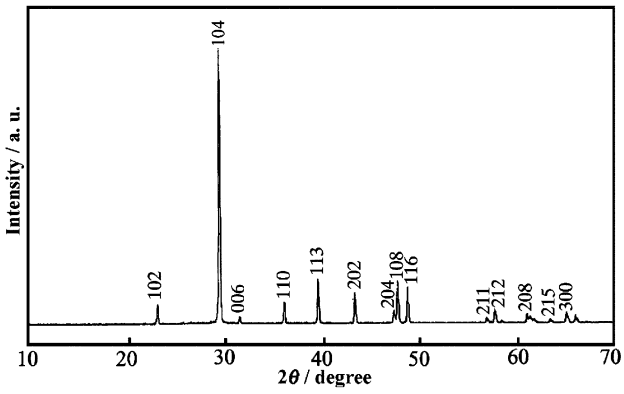

Fig. 1. XRD patterns of the obtained star-shaped calcite microcrystals.

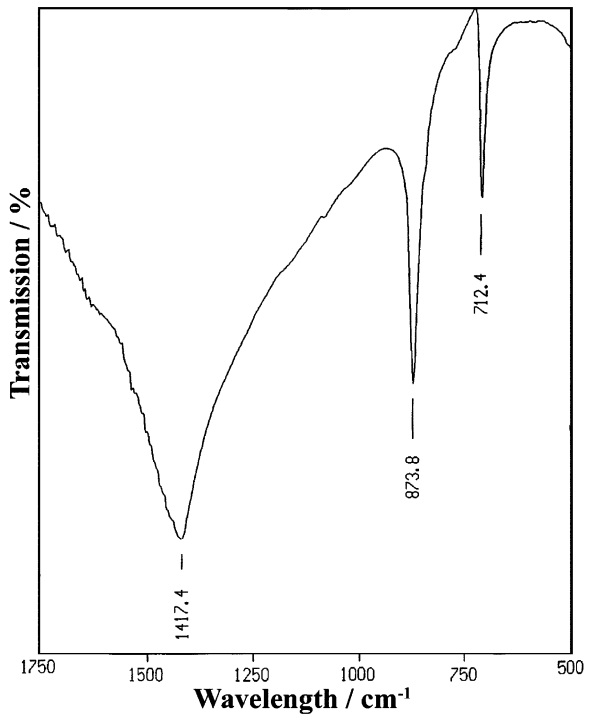

Fig. 2. Infrared spectrum of the obtained star-shaped calcite microcrystals.

the midpoint of six edges not being intersecting with *c*-axis were observed (Fig. 4b). With the reaction process to 4 h, due to the obvious slow growth of six central points of six $\{10\bar{1}4\}$ faces, another six edges intersecting with *c*-axis gradually extruded, resulting in six distinct arms extending radically, which indicates an initial stage of the final star-shaped crystals (as shown in Fig. 4c).

In the presence of Mg^{2+}, calcite crystals with oriented nucleation and growth were reported and it has been established that Mg^{2+} ions exerts a significant influence on phase and morphology of calcium carbonate [16–18]. And in our experiment, we also find Mg^{2+} ions have effect on phase and morphology. The contrast experiment without Mg^{2+} in the mixed solvent of ethanol/H_2O (4:1 vol%) was done and the products were mainly rhombohedral microcrystals with calcite structure and a few of rod-like aragonite crystals concluded from the XRD pattern and the SEM images (shown in Figs. S1 and S2 of Supplementary materials). It can be inferred that Mg^{2+} take effect on the formation of star-shaped calcite crystals, which possibly changes the habit or appearance of crystals.

Crystallographic habit and appearances are well-known to be modified by the selective adsorption of organic molecules or ionic species on specific crystal surface to suppress the regular growth [7,9,22]. Some studies reported Mg^{2+} ions could be accommodated into the calcite structure where it caused a pronounced inhibition of crystal growth, which is also ascribed to the adsorption of Mg^{2+} ions on the special growing crystal sites [23]. Correspondingly, here Mg^{2+} ions can be adsorbed onto the growing crystal surfaces and exerts an important influence on the morphology. Judging from the experimental results, while the introduction of Mg^{2+} changed the general growth habit of calcite, the rhombohedra microcrystals with calcite structure firstly formed with only the $\{10\bar{1}4\}$ family of hexagonal faces, and evolve to the final star-shaped morphology possessing $\bar{3}m$ symmetry. From the SAED pattern of the tip of an arm, it can be judged that the arms of the crystals separately stretch to the six directions perpendicular to the *c*-axis, which indicates that Mg^{2+} ions were specifically absorbed on the planes parallel to the *c*-axis [24]. And Mg^{2+} ions have entered the crystal lattice of calcite to form solid solution [25] and the content of Mg^{2+} ions in the crystal lattice is about 3.44% measured via ICP technique. Thus, due to the presence of large quantity of alcohol in solution, the partially dehydrated Mg^{2+} ions can enter the crystal lattice, which will be absorbed on the crystal planes parallel to *c*-axis more easily, suppressing the regular growth and inducing growth perpendicular to *c*-axis.

In the formation process of calcite with such a novel star-shaped morphology, the solvent also plays an important role. The contrast experiments in H_2O or ethanol were made. In the system of H_2O, besides a very little amount of calcite powders, the products were mainly aragonite, in which many branch-like bulk aragonite crystals with the length of 0.5–1 cm and white luster grow from the solution. Fig. 5a illustrates the XRD patterns of the powders ground from the branch-like bulk crystals. All the diffraction peaks can be indexed to the corresponding orthorhombic phase (JCPDS No. 41-1475). The XRD pattern of several bulk crystals is displayed in Fig. 5b, which indicates that the aragonite crystals grew along the *c*-axis. In the corresponding infrared spectrum (Fig. S3 in Supplementary materials) of the products, recorded over the region from 500 to 1750 cm^{-1} [26], provides further evidence of the pure aragonite composition of the product. Fig. 6a displays the SEM images of the novel branch-like single crystals with aragonite structure. The aragonite microcrystals extends to large ferns with the ca. 2–5 mm in diameter and 0.2–0.5 cm in length issuing from common boughs with the ca. 5–8 mm in diameter and 0.5–1 cm in length. The corresponding section of the bulk single crystals displays a hollow-prism-like morphology (Fig. 6b). The growth axis of the crystals is parallel to the *c*-axis, according to the index of the corresponding SAED patterns (inset of Fig. 6b), which is consistent with the analytical results of XRD.

It is obvious that the aqueous solvent is obviously favorable to the formation of aragonite. Moreover, the corresponding bulk crystals easily grow from the solution under the hydrothermal condition probably because, for the aragonite, such solution remains under the metastable supersaturation, which guarantees the formation of seed crystals and the perfect growth of the bulk crystals. When ethanol was used as the solvent, the products were calcite (XRD pattern shown in Fig. S4 of Supplementary materials) and the corresponding SEM images showed irregular morphology (Fig. 6c).

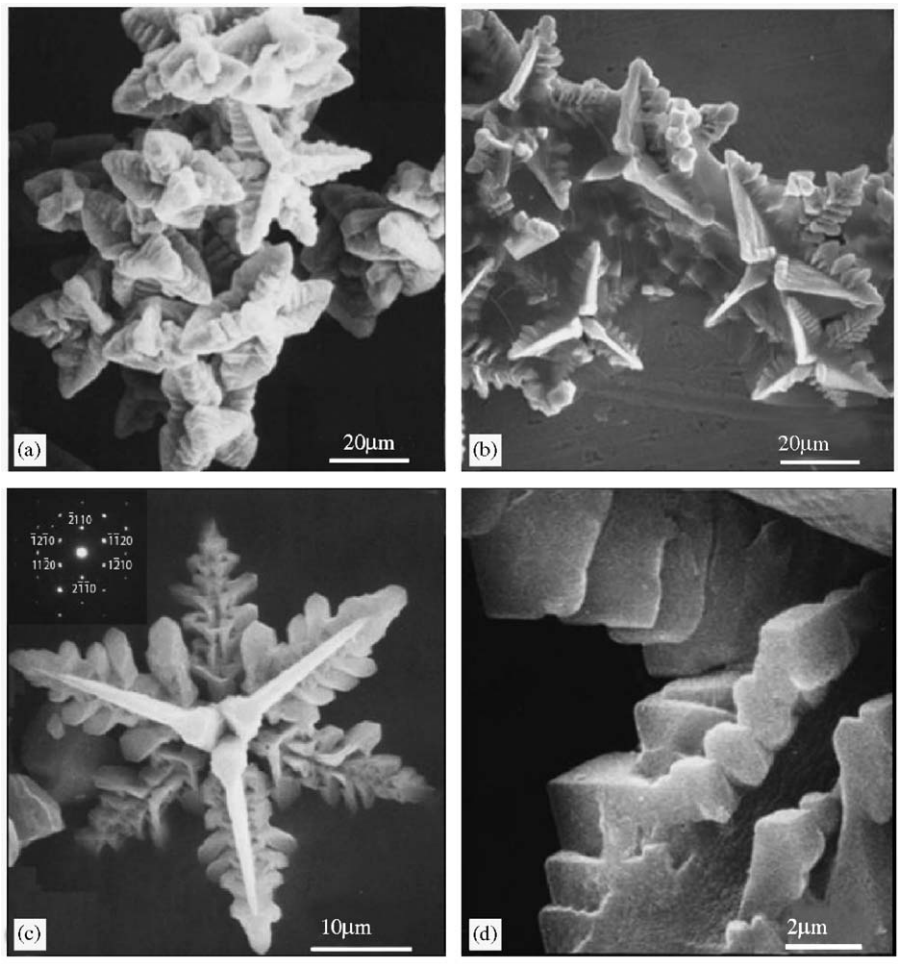

Fig. 3. SEM images of the obtained star-shaped calcite microcrystals: (a) and (b) the large quantity of lateral star-shaped calcites, (c) the frontal images of the star-shaped calcite and SAED pattern from the tip of an arm (the inset), (d) the enlarged image of an arm of the star-shaped calcite.

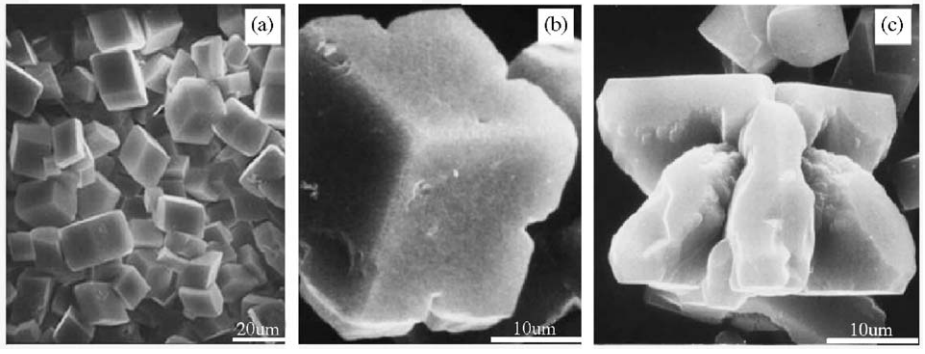

Fig. 4. Morphology evolution of the products at different reaction time: (a) mainly the products of rhombohedra crystals with calcite structure consisting of the basal six {104} planes at the earlier stage for 0.5 h, (b) some crystals with dents appearing at the center of the six edges not intersecting with *c*-axis at the reaction time of 2 h, (c) some crystals with the concaves at the two vertexes through *c*-axis at the longer reaction time of 4 h.

Obviously, from the above results, it can be concluded that the growth of aragonite bulk crystals, a thermodynamically less stable phase of calcium carbonate, can be achieved in H_2O solvent, and with the addition of ethanol, the products tends to convert into calcite from aragonite, and when only ethanol was used as solvent, the products are calcite. It probably results from the different solubility of the reactants. Calcite is the thermodynamically favored phase, and metastable aragonite is favored when the rate of the concentration of the reactants is sufficiently high [27]. In H_2O, for the large solubility of $CaC1_2$ and urea, the nuclei quickly form and the reaction process is dynamic dominant, so the product is aragonite. Oppositely, in ethanol, the nuclei rate is relatively slow owing to the

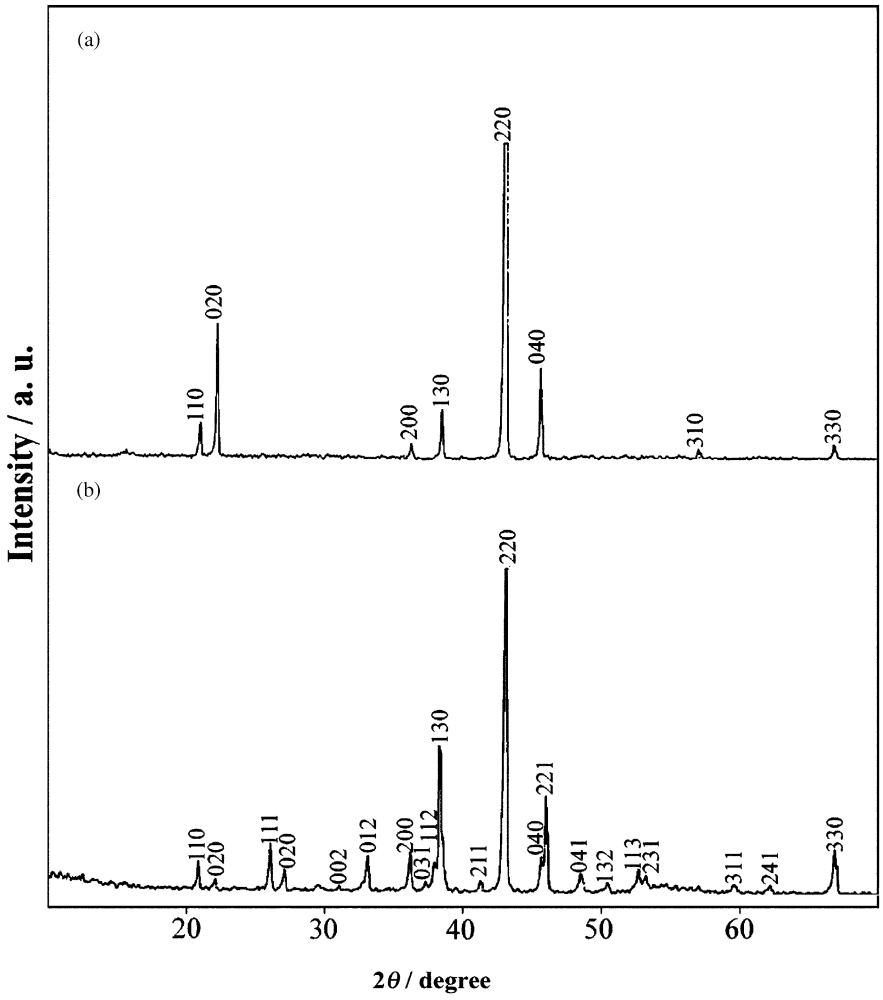

Fig. 5. XRD patterns of the obtained products in aqueous solution: (a) aragonite powder ground from the bulk crystals, (b) several bulk aragonite crystals.

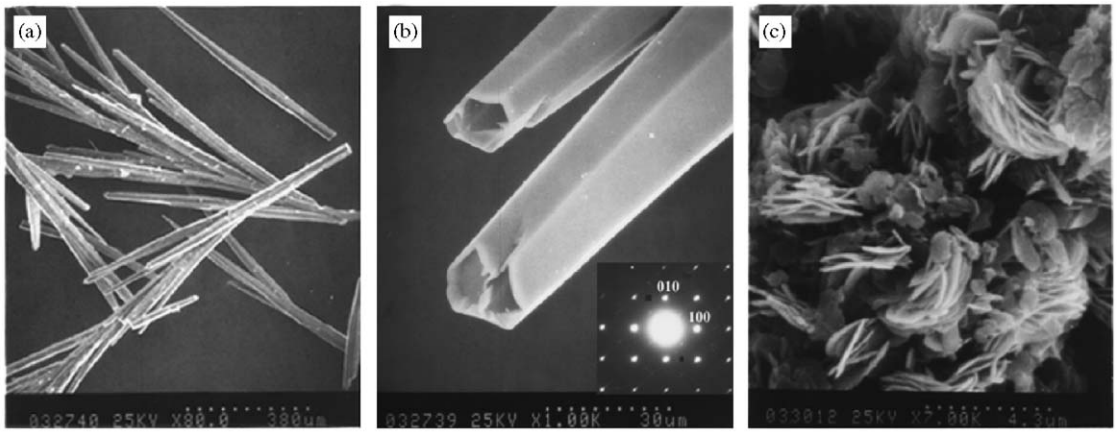

Fig. 6. SEM images of (a) novel branch-like bulk aragonite crystals obtained in aqueous solution, (b) bundle-hollow-prism-like bulk aragonite crystals under higher magnification (inset of the corresponding SAED pattern) in aqueous solution, (c) SEM images of the irregular calcite crystals obtained in ethanol.

sparse reactants, so the thermodynamic product calcite is obtained. Thereby the presence of the ethanol inhibits aragonite nucleation and facilitates thermodynamically controlled nucleation of calcite, which is consistent with the previous report [28]. In addition, the presence of large quantity of alcohol in solution is fovorable to produce dehydrated Mg^{2+} ions, which will enter the crystal lattice to be absorbed on the special plane.

4. Conclusions

The interesting star-shaped calcite crystal with the $\bar{3}m$ symmetry was obtained in the system of ethanol/H_2O (4:1 vol%) with Mg^{2+} ions as inorganic mineralizer under the solvothermal condition. From the experimental analysis, the additive $MgCl_2$ and solvent play important roles in the formation of phase and morphology. Mg^{2+} ions can enter the crystal lattice to be adsorbed on the special planes parallel to *c*-axis, which suppress the regular growth and induce growth perpendicular to *c*-axis. The presence of ethanol promotes thermodynamically controlled nucleation of calcite due to lower solubility than that in water, but also overcomes the strong tendency of magnesium towards hydration.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.01.036.

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