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Sonochemical synthesis of aragonite-type calcium carbonate with different morphologies

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Aragonite, a high-pressure polymorph of $CaCO_3$, was synthesized for the first time from simple $Ca(HCO_3)_2$ solutions by using high-power ultrasound irradiation. XRD, FT-IR and SEM techniques were used to characterize the phase composition and morphology of the products. The intensity of the ultrasound irradiation was found to have a remarkable effect on the morphology of the as-synthesized aragonite. The morphology evolved from rod-shaped to spindle-shaped when the acoustic amplitude is increased from 50% to 70% of the full amplitude. A possible mechanism for the formation of this controllable aragonite formation is proposed. The dissolved CO_2 plays a crucial role in the homogeneous nucleation and growth of aragonite under sonication. Vaterite with flower- or dendrite-like structures could also be obtained by using 75% or 80% of the full acoustic amplitude, respectively. A nonequilibrium kinetics process controls the formation of unstable vaterite with unusual structures.

Introduction

Calcium carbonate exists in three anhydrous polymorphs (calcite, aragonite and vaterite), two hydrous forms (calcium carbonate hexahydrate and calcium carbonate monohydrate), as well as amorphous $CaCO_3$.[1] The phase diagram of calcium carbonate shows that calcite is the stable form under ambient conditions and that aragonite is the high-pressure polymorph.[2,3] Vaterite is thermodynamically unstable.[4] Crystallography investigations show that rhombohedral calcite and hexagonal vaterite possess threefold symmetry axes and their space groups are respectively *R*-3*c* and $P6_3/mmc$, while orthorhombic aragonite crystallizes in the space group *Pmcn* and possesses no such threefold axis. Another distinction of the aragonite structure is that the Ca^{2+} ions have a ninefold coordination, rather than displaying the sixfold coordination of the calcite and vaterite structures. The instability of aragonite under ambient conditions is ascribed to the fact that Ca^{2+} is rather small for ninefold coordination. By contrast, $SrCO_3$, $BaCO_3$ and $PbCO_3$ with aragonite structure are stable owing to the larger cations. Furthermore, the common morphologies of the $CaCO_3$ polymorphs are rhombohedral calcite, needle or rod-like aragonite and spherical vaterite.

Calcium carbonate with the common polymorphs of aragonite or calcite has been applied in industry as fillers and pigments. Recently, sustained interest in aragonite is increasing. Its needle-like crystals are used as fillers for the improvement of the mechanical properties of paper and polymer materials, while paper quality such as printing characteristics, luster and color are greatly influenced by these polymorphs.[5,6] Therefore, polymorphic control of the crystal is very important in industrial processes. Aragonite is also a good biomedical material because it is denser than calcite and can be integrated, resolved and replaced by bone.[7,8]

Currently, controlled morphology studies on $CaCO_3$ polymorphs seem to center on the biomineralization process. The general methodology, recently reviewed by Colfen,[1] is that either soluble polymeric additives are employed in the precipitation process, leading to microparticles with complex shapes that are even partly hybrids of two different polymorphs, or macroscopic templates are used as confined reaction environments for precipitation. However, the production on a large scale of $CaCO_3$ particles with the same morphology and a uniform size still remains a challenge. The inorganic synthesis of metastable aragonite has been invoked many times in the chemical and geological literature. Wary and Daniels gave a detailed description of experimental factors for the synthesis of aragonite by a direct inorganic precipitation method using soluble carbonate and calcium salts as initial materials.[9] Interestingly, their direct precipitation method was not adopted until Katz *et al.* slightly modified the method by adding a small amount of Sr^{2+}.[10–14] In the presence of Mg^{2+}, metastable formation of aragonite in gels was achieved at elevated pressure over a temperature range of 100 to 270 °C.[15] It was also found that under atmospheric pressure and a low temperature range of 0 to 50 °C pure aragonite polymorph could be precipitated out of $Ca(HCO_3)_2$ solutions.[16] This precipitation reaction, however, was kinetically a very slow process. The overgrowth technique has also been used to prepare pure aragonite through introducing a larger amount of aragonite,[14] or some strontianite or wetherite seeds into solutions containing Ca^{2+} and CO_3^{2-}.[17] Recently, Wang *et al.* reported a homogeneous precipitation route to needle-like aragonite by heating urea and calcium salt solutions at 90 °C.[18] Chakrabarty and Mahapatra synthesized aragonite with needle-, cauliflower- or flake-like morphologies by using $CaCl_2$ and Na_2CO_3 solutions under ambient conditions.[19] Furthermore, at low temperatures of 0 to 25 °C and by means of removing CO_2 gas from a $Ca(HCO_3)_2$ solution with bubbling N_2 gas, McCrea synthesized aragonite or a mixture of aragonite and calcite.[20] Tarutani *et al.* synthesized a mixture of calcite and vaterite,[21] whereas O'Neil *et al.* as well as Kim and O'Neil synthesized pure calcite.[22,23] It appears that the pure aragonite phase cannot be precipitated from $Ca(HCO_3)_2$ solution directly. Moreover, most of the synthesis techniques summarized above tend to produce a mixture of $CaCO_3$ polymorphs, need long reaction times or result in particles of irregular shape and size. For industrial applications, it is desirable to develop a facile and fast technique for the synthesis of metastable aragonite with a single phase and uniform particle size and shape.

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Sonochemical processing, which is simple and operates under ambient conditions, has been proven to be a useful technique for the preparation of novel materials with unusual structures and properties. Syntheses of metastable modifications of inorganic compounds using sonochemical methods have also been reported.[24,25] The chemical effect of ultrasound is based on acoustic cavitation, a property that results from the continuous formation, growth and implosive collapse of bubbles in a liquid. The implosive collapse of the bubbles generates local hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. These local hot spots have been shown to have transient temperatures of about 5000 K, pressures of 1800 atm and cooling rates in excess of 10^8 K s^{-1}.[26] These extreme transient high pressures and temperatures may result in the formation of metastable aragonite. This paper describes the direct formation of metastable aragonite from a $Ca(HCO_3)_2$ solution by ultrasound irradiation. Unusual flower-like or dendritic structures of vaterite were also obtained under intense ultrasound irradiation.

Experimental

All starting materials were of analytic reagent grade. Calcium chloride dihydrate was purchased from Merck, while sodium bicarbonate was from Beijing. All chemicals were used directly without further treatment. In a typical experimental procedure, stoichiometric amounts of $CaCl_2{\cdot}2H_2O$ and $NaHCO_3$ were dissolved in 250 ml distilled water to obtain final concentrations of 0.01 M $CaCl_2$ and 0.02 M $NaHCO_3$. CO_2 gas was then bubbled through the solution for about 10 min. This solution was sonicated at ambient temperature for a given time using a high-intensity ultrasonic probe (750 W model Ultrasonic Processor, 13 mm diameter Ti horn, 20 kHz) by employing a direct immersion titanium horn. The titanium horn was inserted into the solution to a depth of 2 cm. During sonication, the temperature of the bulk solution was approximately 70 °C. The precipitate was obtained by filtration using #5 Millipore membranes, which was then rinsed 3 times with distilled water. After a final rinse with acetone, the precipitate was dried in a 80 °C vacuum oven for 12 h. The yields at different acoustic amplitudes and irradiation times were estimated based on the $CaCl_2$ quantity used. Control experiments were carried out as follows: two samples of calcium carbonate were precipitated directly under the same conditions at 70 °C. Another two samples were synthesized using 50% full acoustic amplitude with 45 min irradiation and a 40% full acoustic amplitude with 120 min irradiation, but without bubbling CO_2 gas. The different sets of experimental conditions used are summarized in Table 1.

The phase composition and structure were identified by using a Bruker D8 Advance Power X-ray diffractometer (using Cu Kα $\lambda = 0.15418$ nm radiation) operating at 40 kV and 40 mA, with a graphite reflected beam monochromator and variable divergence slits. The scanning rate was 0.02° s^{-1}. The morphology and size of as-prepared particles were examined by a LEO 1450 VP scanning microscope. Further characterizations were conducted with a Nicolet 560 spectrophotometer with a resolution of 4 cm^{-1}; the KBr pellet method was employed.

Results and discussions

The formation of aragonite is strongly dependent on the intensity of the ultrasound irradiation (*i.e.*, acoustic amplitude).[27] When a ultrasound power of *ca.* 40 watts, was used, a two-phase mixture of calcite and aragonite was obtained either after 45 or 60 min ultrasound irradiation (Table 1). However, when the acoustic amplitude was increased to 50% amplitude, a pure aragonite phase was produced in 45 to 60 min. Acoustic amplitudes ranging from 60% to 70% full amplitude also led to pure aragonite, whereas a principal phase of vaterite with a small amount of aragonite was obtained by means of 75% full amplitude; further raising the acoustic amplitude to 80% resulted in a mixture of vaterite and aragonite. These results confirm that high-intensity ultrasound promotes the formation of metastable aragonite and unstable vaterite. Furthermore, we also estimated the yield of synthesized aragonite based on the quantity of the initial material $CaCl_2{\cdot}2H_2O$. As a general tendency the yield of aragonite increases with applied ultrasound intensity and irradiated time. A 50% acoustic amplitude and 45 min irradiation or a 70% acoustic amplitude and 20 min irradiation gave a greater than 90% yield of aragonite. In this regard, a fast and simple sonochemical method that facilitates the large-scale production of metastable aragonite has been developed. Moreover, a pure calcite sample was also produced from a solution containing 0.01 M $CaCl_2$ and 0.02 M $NaHCO_3$ without bubbling CO_2 gas, using a 40% acoustic amplitude and 2 h irradiation.

The phase identification of the synthesized calcium carbonate was carried out by the powder X-ray diffraction technique. Fig. 1 depicts the typical XRD patterns of calcium

Table 1 Phase composition of the $CaCO_3$ polymorphs obtained under different ultrasound irradiation conditions

Sample	Acoustic amplitude (%)	Ultrasound power/watts	Power density/W cm^{-2})	Irradiation or precipitation time/min	Phase composition[a]
A	40	40	4.2	60	Cal + Arg (58%)
B	40	40	4.2	45	Cal + Arg (60%)
C	50	58	6.1	60	Arg
D	50	58	6.1	45	Arg
E	60	77	8.1	45	Arg
F	60	77	8.1	25	Arg
G	65	88	9.3	45	Arg
H	70	99	10.4	45	Arg
I	70	99	10.4	20	Arg
J	75	113	11.9	20	Vat + Arg (9%)
K	80	128	13.5	20	Arg + Vat (44%)
[b] L				45	Cal + Arg (22%)
[b] M				20	Cal + Arg (20%)
[c] N	50	58	6.1	45	Arg
[c] O	40	42	4.4	120	Cal

[a] Cal, Arg and Vat denote calcite, aragonite and vaterite, respectively; the percentage in parenthesis denotes the percent ratios of the polymorph in the sample estimated from the XRD peak intensity. [b] Without irradiation at 70 °C. [c] Without bubbling CO_2 gas.

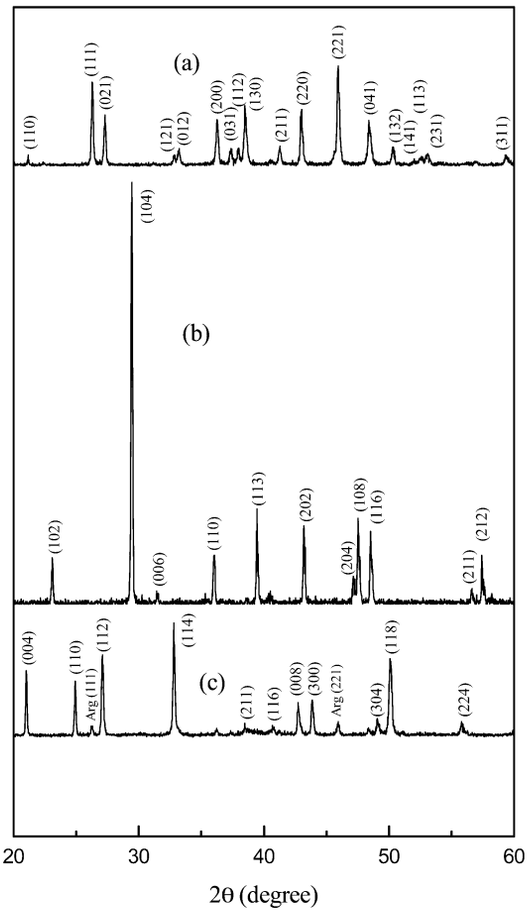

Fig. 1 Typical XRD patterns of calcium carbonate polymorphs synthesized under different conditions: (a) aragonite, sample D, 50% acoustic amplitude, 45 min; (b) calcite, sample O, 40% acoustic amplitude, 120 min; (c) mainly vaterite with a small amount of aragonite, sample J, 75% acoustic amplitude, 20 min.

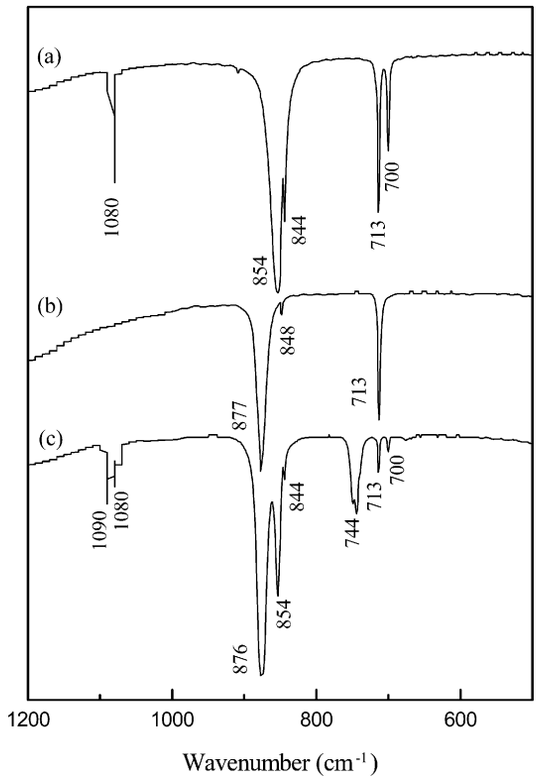

Fig. 2 Typical FT-IR spectra of the calcium carbonate polymorphs: (a) sample D, (b) sample O, (c) sample J.

carbonate polymorphs under different ultrasound irradiation conditions. In comparison with their respective standard JCPDS files (aragonite: 5-0453; calcite: 83-0578; vaterite: 25-0127), the diffraction peaks in trace a in Fig. 1 can be indexed as orthorhombic aragonite with lattice parameters of $a = 4.95900$, $b = 7.96800$, $c = 5.74100$ Å. No characteristic diffraction peaks of calcite at $2\theta = 29.5°$ and of vaterite at $2\theta = 27.0°$, 32.8° can be detected. The diffraction pattern of trace b (Fig. 1) can be assigned to rhombohedral calcite with lattice parameters of $a = 4.98870$ and $b = 17.05290$ Å. Trace c in Fig. 1 reveals a principal vaterite phase with a trace amount of aragonite; the synthesized vaterite is hexagonal, possessing lattice parameters of $a = 7.1500$ and $b = 16.9400$ Å. The sharp and strong peaks also confirmed that the products were well-crystallized.

FT-IR is a useful tool for the identification of calcium carbonate polymorphs.[18,19,28–30] The FT-IR spectra of 3 samples representing the 3 polymorphs are shown in Fig. 2. There are significant differences in the IR spectra. Spectrum a in Fig. 2 shows vibrational bands at *ca.* 1080 and 854 cm^{-1} that can be attributed to the characteristic symmetric carbonate stretching (ν_1 mode) and a carbonate out-of-plane bending (ν_2 mode) vibrations of aragonite, respectively. The pair of bands at *ca.* 713 and 700 cm^{-1} that can be assigned to the in-plane bending modes (ν_4 mode) of aragonite further demonstrate that the as-synthesized aragonite is a single phase.[18,27] For spectrum b (Fig. 2), the bands at 877 and 713 cm^{-1} can be attributed to the ν_2 and ν_4 modes of calcite.[19,28–30] In spectrum c of Fig. 2, the band at *ca.* 744 cm^{-1} (ν_4 mode) is a characteristic vibration band of vaterite.[19,28–30] The broad peak near 1090 cm^{-1} indicates the coexistence of principal phase vaterite and a small amount of aragonite. These results agree well with the XRD measurements.

The morphology of the as-synthesized products was studied in detail by using scanning electron microscopy. Fig. 3 shows the SEM images of aragonite synthesized at different ultrasound intensities. An interesting morphology evolution takes place when the intensity is changed over the range of 50-70% amplitude. At 50% acoustic amplitude, the aragonite (image A) exhibits dispersed rod-shaped structure with a normal crystallographic habit; the rod size is about 10×2 μm with an aspect ratio of 5. Compared with image A, the aragonite derived from 60% acoustic amplitude (image B) consists of a mixture of rod-like and spindle-like shapes; the particles are smaller than those in image A, with a mean dimension of 7×1 μm. However, as the acoustic amplitude was raised to 70% full amplitude, uniform and dispersed 5 μm long spindles of aragonite (image C) would appear. One plausible explanation is that the high ultrasound intensity promotes the nucleation of aragonite crystals and thus the total number of nuclei is increased. Since the same amounts of Ca^{2+} and CO_3^{2-} are now distributed to many more nuclei, the resulting aragonite crystals are shorter in size. The evolution of morphology from rod to spindle can be attributed to the high-power sonication. Previous studies have also demonstrated that ultrasound irradiation can generate a variety of novel materials with unusual structures.[24,31] Jeevanandam *et al.* synthesized needle-shaped lanthanum carbonate by use of high-power ultrasound.[32] This shows that the size and morphology of aragonite can be controlled by high-power ultrasound.

Interestingly, the vaterite synthesized at higher ultrasound intensities has a different morphology as shown in Fig. 4. At 75% full acoustic amplitude, the particles in image A exhibit a flower-like shape with a diameter of about 3 μm. In general, vaterite crystallizes in a spherical morphology.[1,16,33] A similar flower-like structure was also observed by Wang *et al.*[18] in their homogeneous precipitation experiment, as well as by

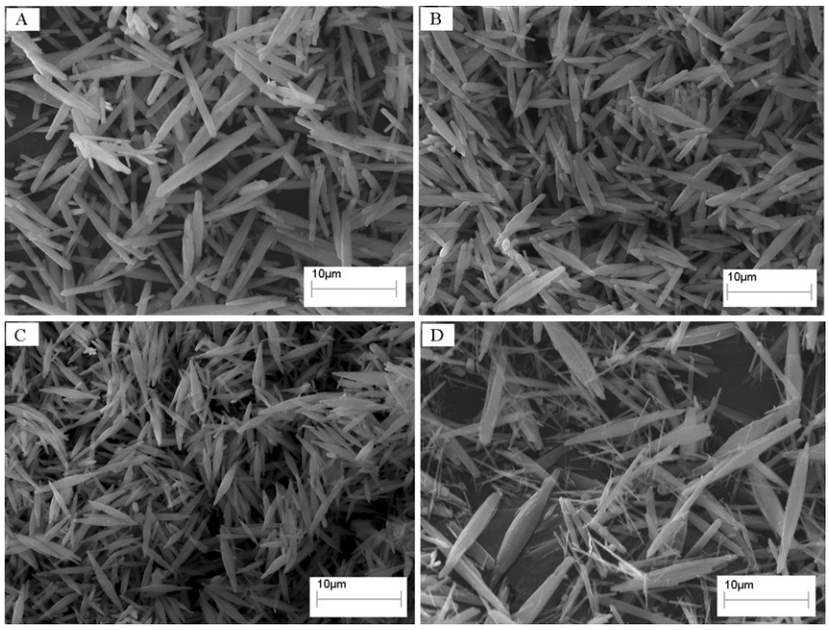

Fig. 3 SEM images of aragonite synthesized at different ultrasound intensities: (A) 50%, sample D; (B) 60%, sample E; (C) 70%, sample I; (D) 50% and without bubbling CO_2 gas, sample N.

Heywood *et al.*[34] and Rudloff *et al.*[35] in the biomimic synthesis. However, in the absence of organic additives, Wang *et al.* obtained a mixture of vaterite and calcite. To the best of our knowledge, the formation of such nearly pure vaterite with a flower-like structure [Fig. 4(A)] in the absence of additives has never been reported. Careful inspection reveals that the flower has an elevated center region, like a pistil. However, when the acoustic amplitude was changed to 80% of full amplitude, a dendrite-structured vaterite was formed, as shown in Fig. 4(B). This unique dendrite structure has never been observed.

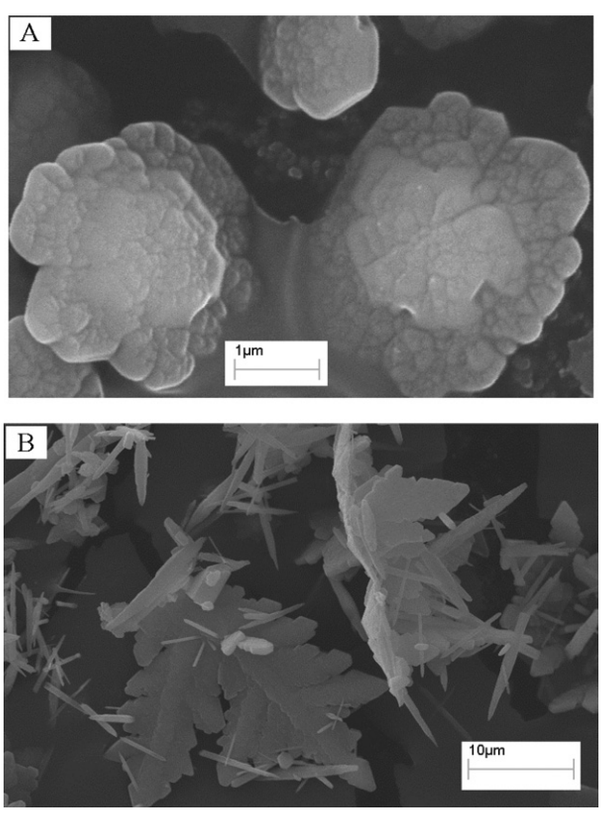

Fig. 4 SEM images of (A) flower-like, sample J and (B) dendrite-like, sample K vaterite.

Two chemical reactions are involved in the formation of calcium carbonate from $Ca(HCO_3)_2$:

$$2HCO_3^- \rightarrow CO_3^{2-} + CO_2 + H_2O \quad (1)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (2)$$

It has been recognized that the formation and evolution of calcium carbonate polymorphs are affected by many factors. These include the Mg^{2+}/Ca^{2+} or Sr^{2+}/Ca^{2+} ratio in solution, the presence of PO_4^{3-} and SO_4^{2-}, salinity and temperature.[6,9–14,16,36] For instance, the presence of inorganic Mg^{2+} or Sr^{2+} and Ba^{2+} ions in solution favors the formation of metastable aragonite. Mg^{2+} stabilizes aragonite by absorbing on the calcite microcrystal surface, thus suppressing the nucleation and growth of calcite. The larger Ba^{2+} and Sr^{2+} ions can incorporate into the aragonite lattice to stabilize the structure. Organic additives have also been used to induce the formation of calcium carbonate polymorphs with complex shapes and to some extend control the phase composition.[1,37] In the current work, no inorganic or organic additives were used. Therefore, sonication must play a crucial role in determining the calcium carbonate phase structure. The effects of ultrasound irradiation on chemical reactions are due to the transient high temperatures and high pressures that develop during the sonochemical cavity collapse by acoustic cavitation.[38] Previous studies documented that aragonite is the high-pressure stable polymorph of $CaCO_3$.[2,3] Intense ultrasound bombardment can certainly provided high-pressure conditions for the formation of metastable aragonite. Ultrasound irradiation also causes translational molecular movement. Such motion, however, is not instantaneous due to the inertial effect. The molecules will experience viscous or frictional interactions and some of the energy will be converted into heat. This heat conversion will inevitably cause a temperature rise in bulk medium.[27] In our experiments, this temperature was measured to be 70 °C. Therefore, a control experiment was carried out in order to check whether this elevated temperature of 70 °C would result in the formation of pure aragonite phase because previous studies showed that elevated temperatures favor aragonite formation.[16] Samples L and M (Table 1) were precipitated directly

from the $Ca(HCO_3)_2$ solutions at 70 °C after bubbling CO_2 gas. XRD analyses show that calcite and a small amount of aragonite coexisted in the samples. This confirms that the elevated temperature of the bulk solution caused by ultrasound irradiation alone could not lead to pure aragonite. In contrast, it is the transient high temperatures and high pressures produced from the acoustic cavitation effect that result in the formation of pure aragonite, confirming the proposed mechanism.

In fact, the dissolved CO_2 (which refers to the sum of H_2CO_3, HO_3^-, CO_3^{2-}, hydrated CO_2 produced by bubbling CO_2 gas) also plays a significant role in the morphology of the as-synthesized aragonite. Another control experiment without bubbling CO_2 gas shows that the aragonite synthesized at 50% full acoustic amplitude consists of bigger spindles and longer rods [Fig. 3(D)], whereas the aragonite synthesized in the presence of dissolved CO_2 is comprised of uniform rods [Fig. 3(A)]. This demonstrates that the dissolved CO_2 gas affects the homogeneous nucleation and growth of aragonite crystal under high-power ultrasound irradiation.

A high ultrasound intensity favors the formation of unstable vaterite. We believe that a nonequilibrium kinetics process determines the formation of unstable vaterite. Under higher acoustic amplitude, reaction (1) would speed up significantly. Therefore, the degree of supersaturation in the solution would increase rapidly, leading to the formation of unstable vaterite. This is consistent with the observation of Kitamura that the proportion of vaterite increases with increasing concentration of CO_3^{2-}.[6] Wang *et al.* obtained the flower-type structure of vaterite by quickly mixing preheated urea and $CaCl_2$ solutions.[18] They thought a higher CO_3^{2-} concentration resulted by preheating the urea solution at 90 °C for 3 h before mixing, caused the formation of flower-type vaterite.

Conclusion

Aragonite with uniform rod- or spindle-like structures can be synthesized from a $Ca(HCO_3)_2$ solution under high-power ultrasound irradiation. The phase structure, morphology and size of the products can be controlled by changing the acoustic amplitude. A 50% to 70% full acoustic amplitude was found to favor the formation of metastable aragonite. This facile route to obtain uniform aragonite is suitable for large-scale industrial production. This approach may also be used to produce other carbonate and oxide materials with novel structures and morphologies.

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