ABSTRACT: Alkaline-earth metal carbonate materials have attracted wide interest because of their high value in many applications. Various sources of carbonate ions (CO$_3^{2-}$), such as CO$_2$ gas, alkaline-metal carbonate salts, and urea, have been reported for the synthesis of metal carbonate crystals, yet a slow and sustained CO$_3^{2-}$ release approach for controlled crystal growth is much desired. In this paper, we demonstrate a new chemical approach toward slow and sustained CO$_3^{2-}$ release for hydrothermal growth of large alkaline-earth metal carbonate single crystals. Such an approach is enabled by the multiple hydrolysis of a small basic amino acid (arginine, Arg). Namely, the amino groups of Arg hydrolyze to form OH$^-$ ions, making the solution basic, and the hydrolysis of the guanidyl group of Arg is hydrothermally triggered to produce urea and ammonia, followed by the hydrolysis of urea to produce CO$_2$ and ammonia and then the release of CO$_3^{2-}$ because of the reaction between CO$_2$ and the OH$^-$ ions hydrolyzed from ammonia. Such a CO$_3^{2-}$ release behavior enables the slow and controlled growth of various carbonate single crystals over a wide range of pH values. The growth of uniform rhombohedron MgCO$_3$ single crystals with variable morphologies and crystal sizes is studied in detail. The influences of reaction temperature, solution pH, precursor type, and concentration on the morphology and size of the resulting MgCO$_3$ crystals are elucidated. The crystal evolution mechanism is also proposed and discussed with various supportive data.

1. INTRODUCTION

Alkaline-earth metal carbonate materials are abundant and have wide applications, such as CO$_2$ sequestration, carriers for drug and functional molecules, biological medicines, refractories, templating synthesis of other materials, and so forth.$^{1-4}$ As a particular example, magnesite (MgCO$_3$) is a rock-forming mineral associated with carbon sequestration in nature.$^5$ MgCO$_3$ is essential in the manufacture of refractories resistant to high temperature and useful as special powder additives or reinforcing agents for various industrial applications. In addition, the biocompatible and nontoxic nature of MgCO$_3$ has rendered them increasingly attractive as a carrier for drug delivery,$^6,7$ as an adsorbent for wastewater treatment,$^8$ as a carrier for sun-blocking semiconductor nanoparticles for cosmetic applications,$^9$ and so forth. Moreover, MgCO$_3$ is an excellent precursor for the postsynthesis of porous magnesium oxides (MgO), which are promising for CO$_2$ capture$^{10,11}$ catalysis,$^{12}$ and wastewater treatment.$^{13-16}$ Therefore, controllable growth of MgCO$_3$ crystals with tailored size, morphology, and structure is desirable.

For crystal growth, the carbonate ion (CO$_3^{2-}$) source and the release rate of CO$_3^{2-}$ in solution are critical for the carbonation reaction with alkaline-earth metal cations. For the synthesis of MgCO$_3$ crystals, several typical methods have been reported. The first one is utilization of CO$_2$ gas as the CO$_3^{2-}$ source. In this way, magnesium carbonate hydrates can be obtained by reacting CO$_2$ gas with Mg(OH)$_2$ suspensions or soluble magnesium salts under alkaline conditions.$^{17,18}$ In such reactions, the mass transfer of CO$_2$ in water is considered as the rate-determining step for growth of MgCO$_3$ because of the low solubility of CO$_2$ in water. The enhanced CO$_2$ gas flow rate and stirring rate can improve the mass transfer of CO$_2$ but without giving the detailed concentration of carbonate ions in solution to characterize the limiting step for the growth of MgCO$_3$. The use of high-pressure CO$_2$ for the reaction with Mg(OH)$_2$ at a high temperature can significantly improve the reaction kinetics to form MgCO$_3$ crystals.$^{19}$ In such reactions, the mass transfer of CO$_2$ in water is considered as the rate-determining step for growth of MgCO$_3$ because of the low solubility of CO$_2$ in water. The enhanced CO$_2$ gas flow rate and stirring rate can improve the mass transfer of CO$_2$ but without giving the detailed concentration of carbonate ions in solution to characterize the limiting step for the growth of MgCO$_3$. 

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ethanol, is necessary in such a tri-phase reaction to facilitate the formation of MgCO₃. The second method is to use soluble inorganic carbonate salts, such as Na₂CO₃ or K₂CO₃, for the growth of MgCO₃. Hydromagnesite products can be produced at low temperatures. These soluble inorganic carbonates dissolve immediately after being added to water; thus, the reactions with Mg²⁺ cations are very fast, which makes it relatively difficult for slow and controlled crystal growth of MgCO₃. The third method is the utilization of soluble organic molecules as the CO₃²⁻ source. In particular, urea is often used because it can be rapidly hydrolyzed to release a massive amount of CO₃²⁻ under non-neutral conditions. The obtained magnesium carbonate hydrates at low temperatures can be transferred to pure MgCO₃ crystals under hydrothermal conditions. Because the hydrolysis rate of urea is so fast, the release and the concentration of CO₃²⁻ ions cannot be well controlled, leading to MgCO₃ crystals with small and non-uniform sizes. Alternatively, Yang et al. have used hexamethylenetetramine as the CO₃²⁻ source, which produces formaldehyde to react with O₂ to produce CO₂, thereby reducing the release rate of CO₃²⁻ and producing micron-sized anhydrous MgCO₃ particles under hydrothermal conditions. However, such a reaction is limited by the content of O₂ in the closed autoclave. In addition, some other special methods have also been reported. For example, in order to obtain larger MgCO₃ crystals, Lou et al. conducted the synthesis in molten sodium at 550 °C. Molten sodium can increase the solubility of MgCO₃ such that the number of crystal nuclei decreases and the size of the particles increases. Based on the analysis of the prior research, it is still highly desirable to develop a slow and sustained CO₃²⁻ release pathway for the controllable growth of large MgCO₃ crystals.

Amino acids (AAs), which are stable and easy to store, have been widely used for the synthesis of organic and inorganic materials. They can not only coordinate with metal ions to form complexes for the structure and composition control but also can play as structure-directing agents to guide the formation of special structures and crystals. In the synthesis of alkaline-earth metal-carbonate crystals, AAs and their polymerized forms (peptides and proteins) have been used to guide the bio-mineralization of CaCO₃ with special polymorphs, such as vaterite microspheres, smooth mineral films, and calcite single crystals. In addition, AAs are small amphoteric molecules. They might modify crystal surfaces and change the crystal growth behavior. Moreover, AAs carry amphoteric molecules. They might modify crystal surfaces and change the crystal growth behavior. Furthermore, until now, there is little exploration of AAs as a source for CO₃²⁻ for the controlled growth of metal carbonate crystals.

Herein, in this paper, by exploring the twenty regular AAs, we report, for the first time, the successful utilization of basic AAs, especially arginine (Arg), to establish a sustained and controlled CO₃²⁻ release approach for the hydrothermal synthesis of uniform and large alkaline-earth metal carbonate single crystals. A series of crystals, including MgCO₃, CaCO₃, BaCO₃, and SrCO₃, can be obtained by this AA-mediated growth method. The synthesis of uniform rhombohedral MgCO₃ single crystals with variable sizes and morphologies are studied in detail. The influences of the hydrothermal reaction temperature and time, solution pH values, the AA type, as well as the magnesium salt type and concentration on the growth of MgCO₃ crystals are elucidated. The mechanism for the formation of the MgCO₃ crystals is explored. The high-temperature-triggered hydrolysis of the guanidyl group of Arg slowly produces CO₂ and OH⁻ ions, thus providing a slow and sustained CO₃²⁻ release pathway for the controllable growth of alkaline-earth metal carbonate single crystals.

2. RESULTS AND DISCUSSION

2.1. Amino-Acid-Mediated Growth of Rhombohedral MgCO₃ Crystals. Uniform rhombohedral MgCO₃ single crystals can be grown from the inorganic salt Mg(NO₃)₂·6H₂O and basic Arg as the CO₃²⁻ ion source with a molar ratio of 1.0 using the controllable amino-acid-mediated hydrothermal growth method at 200 °C for 48 h. The wide-angle X-ray diffraction (XRD) pattern (Figure 1a) shows a group of sharp peaks that can be assigned to various diffraction planes of a hexagonal magnesite (MgCO₃·6H₂O). The direct evidence is the presence of the (104) and (110) diffraction peaks at 200 °C. The high-resolution transmission electron microscopy (HRTEM) image (Figure 2g) reveals that the particle is single crystalline. The d-spacing is estimated to be 3.5 Å, corresponding to the (104) facet of MgCO₃. The corresponding selected-area electron diffraction (SAED)
pattern (Figure 2h) shows the presence of bright spots, which can be indexed to the (104), (110), and (116) facets of MgCO₃ crystals, further revealing that the crystal has a high crystallographic orientation.37

2.2. Influencing Factors on Growth of MgCO₃ Crystals. 2.2.1. Effect of Hydrothermal Temperature. The hydrothermal temperature plays a critical role in controlling the crystal phase and product yield. With the Mg²⁺/Arg molar ratio fixed at 1.0 and the heating time fixed at 48 h, TGA results show that the MgCO₃ yield significantly increases from ∼3.8% at 120 °C to 67.7% at 160 °C and then further to 85.1% at 200 °C (Figure S1A,B). The wide-angle XRD pattern of the sample obtained at 120 °C possesses three weakly crystallized phases, namely, a major brucite Mg(OH)₂ phase (JCPDS Card no. 44-1482), a moderate MgCO₃ phase, and a minor Mg₅(CO₃)₄(OH)₂·4H₂O phase (JCPDS Card no. 25-0513), respectively (Figure 1c). Accordingly, the SEM image of this sample (Figure 2a) shows the coexistence of two significantly different crystal morphologies, namely, nanoflakes of ∼500 nm in dimension and ∼30 nm in thickness that can be assigned to Mg(OH)₂, or Mg₅(CO₃)₄(OH)₂·4H₂O, and small sized (<5 μm) rhombohedral particles assigned to MgCO₃, respectively. With the hydrothermal temperature increased to 160 °C, the wide-angle XRD pattern shows that a predominant MgCO₃ phase can be formed in the resultant sample (Figure 1b). This sample is predominantly composed of rhombohedral MgCO₃ crystals (Figure 2b). Nevertheless, their surfaces are not smooth but attached with many smaller particles, indicating that there are probably some minor crystal impurities or small-sized MgCO₃ crystals. With the temperature further increased to 200 °C, pure and highly crystalline MgCO₃ single crystals can be obtained (Figure 2c). The corners of the MgCO₃ crystals become acute and smooth with no fragments observed on the crystal surfaces (Figure 2d). On the one hand, the crystal size of the MgCO₃ phase increases from ∼29.3 to 60.6 nm with the temperature increased from 120 to 200 °C (Figure S1C). Meanwhile, the overall mean size of the rhombohedral MgCO₃ particles increases from <5 μm at 120 °C to 25.0 ± 0.13 μm at 160 °C and further to 49.6 ± 0.25 μm at 200 °C (Figure S1D). This is because higher temperature results in a high solute oversaturation favoring the growth of large crystals.

2.2.2. Effect of Hydrothermal Time. To investigate the evolution of product species and crystal growth during the hydrothermal process, the hydrothermal time is varied from 1.0 to 48 h with the temperature fixed at 200 °C and the Mg²⁺/Arg molar ratio fixed at 1.0. The wide-angle XRD pattern shows that a pure Mg(OH)₂ phase is present in the sample obtained with a hydrothermal time of 1.0 h (Figure 3a). With the hydrothermal period extended to 3.0 and 6.0 h, a mixed phase composed of a major MgCO₃ phase and a minor Mg(OH)₂ phase can be observed in the resultant two samples (Figure 3b,c). The content of the Mg(OH)₂ phase decreases, while the content of the MgCO₃ phase increases (Figure S2A,B). With the hydrothermal time prolonged to 12 h or longer, the pure MgCO₃ phase can be obtained (Figure 3d−f). The crystal yield and crystallite size both increase with the extension of the hydrothermal time (Figure S2B,C).

SEM images of the products synthesized at different hydrothermal periods further illustrate the evolution of the two phases of Mg(OH)₂ and MgCO₃. The Mg(OH)₂ phase existing in the samples obtained at a hydrothermal time of 1.0−6.0 h has a hexagonal sheet-like morphology (Figure 4a−d). The sheets are of ∼500 nm in lateral size and ∼30 nm in thickness. The MgCO₃ phase with a rhombohedral shape starts to emerge in the sample obtained at a hydrothermal time

Figure 2. SEM (a−f) and HRTEM (g) images and SAED (h) pattern of the samples obtained by hydrothermally treating the Mg(NO₃)₂/Arg (molar ratio 1.0) solution at 120 °C (a), 160 °C (b), and 200 °C (c−h) for 48 h.

Figure 3. Wide-angle XRD patterns of the samples obtained by hydrothermally treating the Mg(NO₃)₂/Arg (molar ratio 1.0) solution at 200 °C for 1 (a), 3 (b), 6 (c), 12 (d), 24 (e), and 48 h (f), respectively.
of 3.0 h (Figure 4b). In addition, there are many sheetlike 
Mg(OH)2 fragments attached on the surfaces of MgCO3 
rhombohedron particles. With the hydrothermal time 
prolonged to 12 h or more, pure uniform MgCO3 
rhombohedron single crystals with smooth surfaces and 
sharp edges can be observed (Figures 4e,f, and 2d). This is 
because the Ostwald ripening process occurs with all the small 
fragments transformed into larger MgCO3 crystals. As a result, 
increase in the crystallite size and particle size of the MgCO3 
rhombohedron crystals can be observed (Figure S2C,D).

2.2.3. Effect of the Initial pH Value. Various samples were 
synthesized at different initial solution pH values (1.0−12.2) 
with the Mg2+/Arg molar ratio fixed at 1.0 and the 
hydrothermal conditions fixed at 200 °C for 48 h. 
Theoretically, with a Mg2+ concentration of 83.3 mmol L−1, 
the pH at which Mg(OH)2 starts to precipitate is about 9.67, 
calculated from the solubility product constant of Mg(OH)2 at 
25 °C. At high initial pH values (10.5, 11.0, and 12.2), white 
precipitates can be observed before the hydrothermal treat-
ment, which can be identified as Mg(OH)2 (Figure S3). After 
the hydrothermal treatment, the pH values decrease to ∼9.5. 
At the low initial pH values (1.0−8.8), no precipitation can be 
observed before the hydrothermal treatment. After the 
hydrothermal treatment, the pH values increase to 7.8−9.2. 
After the hydrothermal treatment, pure MgCO3 crystals can be 
obtained at a wide pH range of 1.0−11.1 (Figure 5). Only a 
higher initial pH value of 12.2 results in a mixed phase of 
MgCO3 and Mg(OH)2 with a mass ratio of about 3 (Figure 
S4A). The formation of MgCO3 at all the pH values indicates 
the occurrence of gradual release of CO3 2− ions from Arg. The 
yield of MgCO3 increases from 26.5% at pH 1.0 to 83.6% at 
pH 11.0 (Figure S4B). This is because the formation of CO3 2− 
ions from Arg and precipitation are hindered at low pH values. 
With a low initial pH value, the nucleation and growth can be 
slowed down, leading to the growth of MgCO3 crystals with an 
enhanced crystallinity and a significantly enhanced mean 
particle size up to 121 ± 0.6 μm (Figures 5, and S4D). In a 
strongly alkaline environment (initial pH 12.2), part of the 
Mg2+ ions prefer to form Mg(OH)2 instead of MgCO3 because 
the high OH− concentration can shift the reaction equilibrium 
to the Mg(OH)2 direction which is caused by the lower 
Kθ value of Mg(OH)2 compared with that of MgCO3. 
SEM image shows that the MgCO3 sample obtained at pH 
1.0 presents a spherical rhombohedron morphology with 
rounded corners (Figure 6a). The crystal rounding may be 
resulted from the interactions between Mg2+ ions on the crystal 
surface and organic molecules carrying negative charges under
strongly acidic conditions. With initial pH values of 3.2–11.0, all the obtained MgCO₃ samples show a rhombohedral morphology with sharp edges and exposed (104) facet (Figure 6b–e). The overall particle size increases from 39.5 to 121 μm with the initial pH value decreased from 11.1 to 1.0 (Figures 6a–e, and S4D), indicating that the release of CO₃²⁻ can be well controlled, and low pH values are favored for the growth of large crystals. The sample grown at pH 12.2 exhibits an irregular crystal morphology with a large number of fractions (Figure 6f). The preferred growth of the (104) facet may be inhibited under strong alkaline conditions, while the other crystal planes are selected to grow, as revealed by the intensified (006) facet (Figure 5).

2.2.4. Effect of Precursor Concentration. The precursor concentration is an important factor to control the crystallization kinetics and the morphology of resultant crystals. Three different precursor concentrations (41.7, 83.3, and 167 mmol L⁻¹) were adopted with the Mg²⁺/Arg molar ratio fixed at 1.0 and the hydrothermal treatment conditions fixed at 200 °C for 48 h. In all cases, the pure MgCO₃ crystal phase can be obtained (Figure S5). The crystallite size decreases slightly from 61.1 to 57.6 nm and the overall particle size also decreases from 49.9 to 35.7 μm with the increase of the precursor concentration (Figure S6B,C). This phenomenon is because the nucleation rate is faster at a higher precursor concentration, leading to the growth of a large number of smaller particles. All the samples obtained with different precursor concentrations possess the rhombohedral single crystal morphology (Figure S7A,B). It is observed that a higher precursor concentration results in more crystal fragments attached on the surfaces of the rhombohedral crystals.

In addition, the Mg²⁺/Arg molar ratio was also varied. Theoretically, a Mg²⁺/Arg molar ratio of 1.0 can result in 100% conversion of the Mg²⁺ cations to metal carbonate, provided that the guanidyl group of Arg can be fully hydrolyzed to form CO₃²⁻ ions, and these ions can be fully utilized. Practically, a maximum of ~85.1% carbonation of the Mg²⁺ cations can be achieved with a Mg²⁺/Arg molar ratio of 1.0. A lower Mg²⁺/Arg molar ratio of 0.67 can give a higher conversion (92.2%) of the Mg²⁺ cations because a higher relative concentration of Arg can produce more CO₃²⁻ ions. In this case, the obtained sample is composed of the pure MgCO₃ phase with a uniform and smooth rhombohedral crystal morphology (Figures S5, S7C). The crystallite size is estimated to be ~58.5 nm, slightly smaller than that (~60.6 nm) of the sample obtained at a molar ratio of 1.0 (Figure S6B), which is due to the higher concentration of CO₃²⁻ ions, resulting in faster nucleation rate and smaller crystallites.

2.2.5. Effect of Various Magnesium Salts. With the Mg²⁺/Arg molar ratio fixed at 1.0 and the hydrothermal treatment conditions fixed at 200 °C for 48 h, pure MgCO₃ crystals with similar rhombohedral single crystal morphology can also be obtained with the use of MgCl₂·6H₂O and MgSO₄ as the precursors (Figures S8–S10). The overall particle size for the sample obtained from the sulfate salt is slightly smaller, and the crystal corners of this sample are more rounded compared with the other two samples obtained from the nitrate and chloride salts. Some recent studies showed that SO₄²⁻, a bivalent anion, can reduce the rate of ripening, via adsorption of sulfate ions onto crystal surfaces. The sulfate adsorption can partially poison the nucleation sites on growing crystals and decrease the rate of growth, thus causing the formation of smaller-sized crystals with sleek rounded corners.

2.2.6. Effects of the Amino Acid Type. Typical basic AAs (His and Lys) and acidic AAs (Asp and Glu) were also adopted to mediate the crystal growth at 200 °C for 48 h. With His as a precursor, the obtained product shows a crystalline MgCO₃ phase and an amorphous carbon phase with a broad diffraction peak at 15–30° (Figure S11). The product is composed of microspheres of ~6 μm in size (Figure 7a,b). The formation of such a product is because His can be hydrothermally carbonized to microspheres and release CO₃²⁻ ions. The microspheres act as the growth template for MgCO₃ crystallization. With Lys as the precursor, the obtained product consists of two crystal phases, Mg(OH)₂ and MgCO₃ (Figure S11). The MgCO₃ phase only accounts for 27.1 wt % (Figure S12). The product shows a 3D flower-like structure of ~3 μm in size, which is assembled from nanosheets of ~30 nm in thickness (Figure 7c,d). The abovementioned result indicates that the release amount of CO₃²⁻ from His and Lys is much lower. On the other hand, no precipitation can be observed using Asp and Glu after the hydrothermal treatment. Even by adjusting the initial pH value to 10.4 before the hydrothermal reaction, only a small amount of Mg(OH)₂ precipitation can be generated (Figure S11). This result indicates that no CO₃²⁻ ions can be released from decarboxylation of acidic AAs in the adopted experimental conditions.

2.3. Discussion on the Growth Mechanism and the Key Influencing Factors. Based on the abovementioned results, Arg is essential to mediate the growth of MgCO₃ single crystals by gradual and sustained release of CO₃²⁻ ions. The chemical reaction mechanism guiding the formation of MgCO₃ is proposed and discussed in detail (Scheme 1, and eqs 1–9).

Prior to the hydrothermal treatment, the hydrolysis of the amino groups of Arg (eq 1) causes the mixed solution to be
alkaline with an initial pH value of 10.5, which leads to the formation of a small amount of the Mg(OH)$_2$ precipitate (eq 2). During the hydrothermal treatment process, the guanidyl group of Arg starts to hydrolyze slowly to generate ammonia and urea (Scheme 1a and eq 3). Ammonia continues to hydrolyze to produce OH$^{-}$ ions (eq 4) so that more Mg(OH)$_2$ precipitate can be produced (Scheme 1b). This explains the facts that Mg(OH)$_2$ is the major or the only phase of the products obtained with a low temperature (Figure 1c) and/or a short hydrothermal time (Figure 3a). With the enhancement of temperature and/or prolonging of hydrothermal time, more guanidyl groups of the Arg molecules are hydrolyzed. Meanwhile, hydrolysis of the produced urea is continuously proceeded to generate CO$_2$ and more ammonia (eq 5). Then, CO$_2$ reacts with the OH$^{-}$ ions hydrolyzed from ammonia to generate CO$_3^{2-}$ ions (eq 6). As a result, precipitation of Mg(OH)$_2$ stops, and Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O and MgCO$_3$ start to form once the concentration products exceed their $K_{\text{sp}}$ values (Scheme 1c, and eqs 7 and 8). As Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O is thermodynamically unstable, it is only a very minor phase at a low hydrothermal temperature and can be converted to the thermodynamically more stable MgCO$_3$ phase. With the continuous hydrolysis and production of CO$_2$, Mg$^{2+}$ and OH$^{-}$ ions are gradually consumed. As a result, the MgCO$_3$ crystals gradually grow larger (Scheme 1d). Simultaneously, the preformed Mg(OH)$_2$ can be gradually dissolved (eq 2 shifting to left), attached to the surface of the formed MgCO$_3$ crystals and converted to MgCO$_3$ (Scheme 1d). Once the hydrolysis of Arg and its product urea is complete, the Mg(OH)$_2$ phase completely disappears, and the CO$_3^{2-}$ and Mg$^{2+}$ ions are stoichiometrically converted to MgCO$_3$ crystals (Figure 3d). To support the gradual and sustained hydrolysis of Arg, as shown in eqs 1 and 3–6, by hydrothermally treating an Arg solution alone at 200 °C, the produced amount of CO$_3^{2-}$ ions from Arg gradually increases with the increase of the hydrothermal time, and the total released amount is identical to the theoretical value (Figure 8). Meanwhile, the final total produced amount (0.23 mol L$^{-1}$) of NH$_4^+$/NH$_3$ is indeed three times of the amount of CO$_3^{2-}$ ions, indicating gradual and complete hydrolysis of the guanidyl group of Arg. In addition, the pH value of the mixture is lowered to ∼9.0, and the yield of the MgCO$_3$ crystals is up to ∼85.1%. After the chemical conversions are complete, during the final stage of the hydrothermal treatment, an Ostwald ripening process occurs with all the small crystal fragments disappeared and transformed into larger MgCO$_3$ crystals, leading to the preferential growth of smooth and orientated crystal facets, which can fill up the edges of the crystals and then sharpen the corners to produce smooth rhombohedrons (Scheme 1e,f).

\[
\text{Mg}^{2+}(aq) + 2\text{OH}^{-}(aq) \rightleftharpoons \text{Mg(OH)}_2(s) \quad (2)
\]

\[
K_{\text{sp}}^{\text{Mg(OH)}_2} = 1.8 \times 10^{-11}
\]

\[
\text{NH}_4^+(aq) + \text{H}_2\text{O} \rightleftharpoons \text{OH}^{-}(aq) + \text{NH}_3(aq) \quad (4)
\]

\[
\text{CO(NH}_2)_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2(aq) + 2\text{NH}_3(aq) \quad (5)
\]

\[
2\text{OH}^{-}(aq) + \text{CO}_2(aq) \rightleftharpoons \text{CO}_3^{2-}(aq) + \text{H}_2\text{O} \quad (6)
\]

\[
\text{Mg}^{2+}(aq) + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{MgCO}_3(s) \quad (7)
\]

\[
K_{\text{sp}}^{\text{MgCO}_3} = 3.5 \times 10^{-8}
\]

\[
5\text{Mg}^{2+}(aq) + 4\text{CO}_3^{2-}(aq) + 2\text{OH}^{-}(aq) + 4\text{H}_2\text{O} \rightleftharpoons 5\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot4\text{H}_2\text{O}(s) \quad (8)
\]

\[
K_{\text{sp}}^{5\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot4\text{H}_2\text{O}} = 1.7 \times 10^{-37}
\]

\[
\text{NH}_3(aq) + \text{H}^+(aq) \rightleftharpoons \text{NH}_4^+(aq) \quad (9)
\]
An intriguing aspect of the growth method is that the slow and sustained generation of CO$_3^{2-}$ ions leads to the controllable growth of large MgCO$_3$ single crystals. Because the CO$_3^{2-}$ ions are generated slowly in situ and a large amount of the Mg$^{2+}$ ions are first precipitated to Mg(OH)$_2$, the concentrations of the two ions are relatively low over the reaction process. Therefore, the solute oversaturation is low, and thus, the nucleation rate is slow. Once MgCO$_3$ nucleus and small crystals are formed, the Mg$^{2+}$ and CO$_3^{2-}$ ions are gradually adsorbed to the (104) facet of the MgCO$_3$ crystals and grow continuously, resulting in the formation of large rhombohedron MgCO$_3$ single crystals. In a control experiment, the spherical MgCO$_3$ single crystals show a hexagonal pyramids, and the size of the prism is mainly 50 $\mu$m (Figure 10c,d). The SrCO$_3$ sample possesses a pure strontianite phase (Figure 9c). The SrCO$_3$ crystals show a hexagonal prism morphology ended with two hexagonal pyramids, and the size of the prism is mainly 50 $\mu$m (Figure 10c,d). The SrCO$_3$ sample possesses a pure strontianite phase (Figure 9c). The SrCO$_3$ crystals show a hexagonal prism morphology ended with two hexagonal pyramids, and the size of the prism is mainly 50 $\mu$m (Figure 10c,d).
3. CONCLUSIONS

In summary, this work offers a novel approach for controllable hydrothermal growth of large alkaline-earth metal carbonate single crystals with variable crystal sizes. The key to the synthesis is the slow and sustained release of CO$_3^{2-}$ ions from AAs mediating the crystal growth rate. Most importantly, the amino group of Arg is hydrolyzed to make the solution alkaline, and the guanidyl group hydrolyzes slowly to produce ammonia and urea, followed by the hydrolysis of urea producing CO$_2$ and more ammonia and then the release of CO$_3^{2-}$ via the reaction between CO$_2$ and OH$^-$ ions hydrolyzed from ammonia. Such a CO$_3^{2-}$ release behavior allows the slow and controlled growth of various single crystals including MgCO$_3$, CaCO$_3$, BaCO$_3$, and SrCO$_3$. The typical MgCO$_3$ products show a single crystalline rhombohedron morphology with uniform and controllable micron sizes (30.0–121 μm). A temperature of ≥160 °C is essential to trigger the CO$_3^{2-}$ release reaction for carbonation and MgCO$_3$ crystal formation. Over the crystal growth process, the Mg$^{2+}$ ions are first partially converted to Mg(OH)$_2$, and then, Mg$_x$((CO$_3$)$_y$(OH)$_z$)$_{4-x}$$·$4H$_2$O forms, followed by the growth of anhydrous MgCO$_3$ crystals. With the prolonging of the hydrothermal treatment, all the Mg$^{2+}$ ion sources can be converted into MgCO$_3$, and the Ostwald ripening process can make the crystals larger with smooth and sharpened corners. MgCO$_3$ single crystals with various sizes and morphologies have been obtained by varying the magnesium salt type, AAs type, precursor concentration, and solution pH values. The solution pH value shows the most significant influence with a lower pH value favored for the slow growth of larger crystals. The findings in this paper may provide new insights into the hydrothermal decomposition of AAs and establish a general protocol for the synthesis of other metal carbonates and their derivative metal oxides.

4. EXPERIMENTAL SECTION

A series of alkaline-earth metal carbonate crystals can be obtained using the AA-mediated growth method. The synthesis of MgCO$_3$ was studied in detail. The details about the chemicals used for the synthesis can be found in the Supporting Information. In a typical synthesis process of the rhombohedron MgCO$_3$ crystals, 1.28 g of Mg(NO$_3$)$_2$·6H$_2$O (5.0 mmol) and 0.87 g of Arg (5.0 mmol) with a molar ratio of 1.0 were sequentially dissolved into 60 mL of ultrapure water in a 100 mL beaker. The aqueous mixture with a pH value of 10.5 was transferred into a 100 mL Teflon-lined stainless-steel autoclave, placed in an oven at ambient temperature, and then heated to a specific temperature for the hydrothermal treatment for a certain period. The temperature was varied between 120 and 200 °C, and the heating time was varied between 1 and 48 h to study the crystallization process with the formation of different crystals. After cooling to room temperature, the precipitate was collected by filtration and washed three times with ultrapure water and ethanol. The precipitate was then dried at 60 °C under vacuum overnight. A series of experimental parameters were considered for the synthesis. First, because the mixed solutions of Mg(NO$_3$)$_2$·6H$_2$O and Arg were basic, to avoid the formation of Mg(OH)$_2$ precipitation at the initial mixing stage and to study the influence of the pH value on crystallization, a range of pH values from 1.0 to 12 were adopted for the synthesis. Second, different Mg$^{2+}$ and Arg concentrations with the fixed Mg$^{2+}$/Arg molar ratio of 1.0 were adopted for the synthesis. Third, various magnesium salts were also adopted for the synthesis with the Mg$^{2+}$/Arg molar ratio fixed at 1.0. In addition, several other basic AAs including lysine (denoted as Lys) and histidine (denoted as His) and acidic AAs including glutamic acid (denoted as Glu) and aspartic acid (denoted as Asp) (their molecular structures are shown in Scheme S1) were also adopted to try to synthesize magnesium carbonates. A Mg$^{2+}$/AA molar ratio of 1.0 for Lys and His, and 2.0 for Asp and Glu were adopted. In all the above experiments, the temperature was set at 200 °C, and the heating time was fixed at 48 h.

In addition, in order address the versatility of the synthesis method, a series of other alkaline-earth metal (Ca, Ba and Sr) carbonate crystals were also synthesized using their nitrate salts and Arg with a molar ratio of 1.0. The synthesis process was the same as that for the synthesis of MgCO$_3$ as described above. The conditions were fixed at a heating temperature of 200 °C and a heating time of 48 h.

A series of techniques were adopted to characterize the physicochemical properties of the obtained samples. The details about the characterization and measurement can be found in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01719.

Analyses on the composition, crystallites and particle sizes, and additional XRD, SEM characterization of the products obtained at different conditions (PDF)

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Notes

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