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Original Research Paper

Crystallization of aragonite $CaCO_3$ with complex structures

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ABSTRACT

In this work, aragonite $CaCO_3$ with complex morphologies was synthesized through homogeneous precipitation, in which calcium acetate and urea precipitated at 90 °C in the presence of PVP. The effect of the concentration of urea and PVP on the $CaCO_3$ crystalline was investigated. The morphology and structure of the $CaCO_3$ particles were characterized by SEM, XRD, and FT-IR. It was found that the concentrations of urea and PVP in the mixed aqueous solution were turned out to be important parameters for the morphology of $CaCO_3$ particles. All $CaCO_3$ particles were mainly aragonite with morphology from bundles of rods, bouquet-like and dumbbell-like. And there was no phase transition under the research conditions. Moreover, the possible process for the formation of the morphology of aragonite was discussed.

1. Introduction

Aragonite is a metastable polymorph of calcium carbonate under all geologic conditions. It is a mineral of common occurrence and is known to have very high mechanical strength [1]. A classical example is that the nacreous layer of mollusk shells has higher-order architectures composed of aragonite and organic macromolecules [2,3]. The nacre layer is 3000 times tougher than aragonite alone [4,5]. So controlling materials synthesis at both the molecular and macroscopic levels has attracted much attention. Many approaches have been widely tried to mimic the biological synthesis of aragonite [6–9]. The aragonite crystals were initially separated from the hot solution saturated with carbon dioxide, or by addition of calcium chloride to a hot solution of ammonium or sodium carbonate, when calcium carbonate crystallized [10]. Water-soluble additives, such as, inorganic metal ions [11,12], surfactants [13,14], and polymers [15–17], have been widely used to modify the shapes and control the nucleation and growth of aragonite particles. In order to synthesize needle-like aragonite, some inorganic additives which contained ions, such as Sr^{2+}, Ba^{2+}, Pb^{2+} and Mg^{2+}, have been introduced to the solutions or gels of soluble calcium salts for aragonite growth at ambient or elevated temperature conditions [11,12]. The pure aragonite crystals were obtained in 70 °C solution by precipitation of soluble carbonate and calcium salts [18]. Then, at the controlled conditions aragonite crystals can be manipulated in the process of crystallization. Generally, higher temperature, low concentration and low addition rate of salt carbonate solution were favorable to the formation of aragonite [19,20]. Typically, the aragonite whiskers were assisted by cetyltrimethylammonium bromide (CTAB) [12]. The rods of aragonite were fabricated with 50% water and 50% pyridine as solvent [21]. And the uniform needle-like aragonite particles were obtained by aging solutions of calcium salts in the presence of urea at 90 °C by Matijević et al. [22]. While Yu and co-workers synthesized pure aragonite crystals with rod-like shape in aqueous solution of 1:3 ratio of ethol to water, and dumbbell-like crystals made of aragonite nanorods with 1:1 ratio of ethol to water without any organic additives [23].

Nature is extremely advanced in controlling over the crystallization of inorganic materials by the process of biomineralization, resulting in organic–inorganic hybrid materials with complex shape, hierarchical order and yet cost-effective strategy [24]. Thus, mimicking complex structures produced by nature in the laboratory may have a significant impact on the development of new composite materials. Pure aragonite with urchin-like micropatterns has been prepared in the presence of sodium dodecyl benzenesulfonate (SDBS) [25], and the aragonite with needle-, cauliflower- or flake-like morphologies was produced by using $CaCl_2$ and Na_2CO_3 solutions at the ambient temperature [26]. Also, the chrysanthemum-like or needle-like aragonite was synthesized from sparingly soluble calcium salts [27]. In the present work, the pure phase of aragonite crystals with morphology from rod-like to complex dumbbell-like superstructures was mineralized in the presence of poly(N-vinyl pyrrolidone) (PVP), which is a water-soluble and uncharged biomaterial under mild conditions (90 °C). PVP has been applied as shape-control reagents for the synthesis

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of inorganic materials, and various complex structures [28–30]. Likewise, the vaterite crystal, a metastable polymorph of $CaCO_3$, was obtained by precipitation of soluble carbonate and calcium salts in the presence of PVP [31,32]. In this work, aragonite superstructure was synthesized by homogeneous precipitation route, in which calcium acetate and urea precipitated at 90 °C in the presence of PVP. The morphology and complex structure of the aragonite particles were examined by scanning electron microscopy (SEM), X-ray diffractometry (XRD), Fourier transform infrared spectrometry (FT-IR), thermogravimetric and differential scanning calorimetry (TG/DSC), with an aim that the complex aggregate is elucidated.

2. Experimental

2.1. Materials

All starting materials, calcium acetate ($Ca(CH_3COO)_2$), urea ($CO(NH_2)_2$) and poly(N-vinyl pyrrolidone) (PVP, $M_W = 10{,}000$), were of A.R. grade and obtained from Tianjin Fuchen Chemical Ltd. (China). The water used in this work was deionized water.

2.2. Synthesis procedure

The $CaCO_3$ precipitation was preformed by aging solution of calcium acetate in the presence of urea and PVP in a 90 °C bath as described as by Matijević group [22]. Specifically, equal volumes of $Ca(CH_3COO)_2$ solution and urea solution were firstly mixed at room temperature, and PVP was introduced to the solution. After mixed mixing thoroughly, the transparent solution was transferred into a 100 mL color comparison tube. Then, the tube was incubated and unstirred in a 90 °C water bath for 24 h. All of the particles nucleated and grew inside the solution, not on the wall of the flask. Subsequently the solution was quenched to room temperature and the obtained solid was filtered using 0.2 μm cellulose nitrate/acetate membrane. The precipitate was finally dried in a vacuum oven overnight at 60 °C. The synthesized condition of the calcium carbonate particles and that of comparison with sample U of Matijević's work in Ref. [22] was are listed as in Table 1. The concentration of $Ca(CH_3COO)_2$ was kept at 2.0 M, and the concentration of $CO(NH_2)_2$ was varied from 4.0 to 10.0 M, the concentration of PVP ranged from 0 to 5.0 mM.

2.3. Characterization of the particles

The morphology and size of as-prepared particles were examined by S-3400N scanning electron microscope (SEM) operating at an accelerating voltage of 20 kV after sputtered gold film. The aspect ratio of particles was obtained by analysis 100 of particles using Morphologi G2 (Malven) instrument and its software. The phase composition and structure were identified by X-ray diffraction (XRD) recorded on a (Shimadzu XRD-7000) X-ray powder diffractometer with Cu Kα radiation ($\lambda = 1.5405$ Å) at a scanning rate of 10° min^{-1}. The mean grain size D was determined from Scherrer's equation ($D = K\lambda/\beta\cos\theta$, where K is a dimensionless constant, 2θ is the diffraction angle, λ is the wavelength of the X-ray radiation (1.5405 Å), and β is the full width at half-maximum of the diffraction peak). Infrared spectra were collected by using a Bruker Vertex-70 (Germany) Fourier transform infrared (FT-IR) spectrometer on KBr pellets. The thermal behavior of the powders was performed on Netzschsta 449C thermo-analyzer instrument in a Pt–Rh + Al_2O_3 pan, with a heating rate of 10 °C min^{-1} under the flow of Ar gas.

3. Results and discussions

The SEM images of the fabricated $CaCO_3$ crystals with 2 M of $Ca(CH_3COO)_2$ and 2.5 mM of PVP, in varied concentration of $CO(NH_2)_2$ were are shown as in Fig. 1. All pictures in Fig. 1 showed that the prepared $CaCO_3$ particles exhibited rod-like and/or its cluster structures. The rod- or needle- like structures were typical one of aragonite. When the concentration of $CO(NH_2)_2$ was 4.0 M, the rod-like aragonite with about ~5.7 of aspect ratio (defined as the ratio of length to diameter) was obtained as Fig. 1(1#), from which some of the rods showed the tendency of orientation and aggregation with one end for bundle-like structure. Fig. 1(2#) exhibits majority of aragonite crystals with clavate bundle-like structure, made of rods approximately with 8.9 of aspect ratio in addition to minority of rod-like crystals, with 6.0 M concentration of $CO(NH_2)_2$. The bundle-like crystals were formed through end-linkage of rods. With the concentration of urea increased to 8.0 M, the bundle-like crystals aggregated into two kinds of morphology, i.e. bouquet-like or and dumbbell-like structure, composed of aragonite rods, as shown in Fig. 1(3#). Then, the lager bouquet-like and dumbbell-like crystals were observed in Fig. 1(4#), with 10.0 M of $CO(NH_2)_2$.

The above structures were demonstrated by the XRD patterns in Fig. 2. In comparison with the standard JCPDS files (aragonite: 41-1475; calcite: 05-0586; and vaterite: 33-0268), all of the diffraction peaks in the XRD patterns clearly showed the peaks corresponding to *h k l* of 1 1 1, 0 2 1, 0 1 2, 2 0 0, 1 3 0, 2 1 1, 2 2 0, 2 2 1 et al., which agreed with those of aragonite phase. No other polymorph of $CaCO_3$ was detected in the XRD pattern. The sharp and strong peaks indicated that $CaCO_3$ was well crystalline, which is in good accordance with the SEM results shown in Fig. 1. Scherrer's equation was applied to (1 1 1) (2 0 0) (2 2 1) peaks and provided a mean grain size D in Table 1. Table 1 shows the average crystalline size for the prepared $CaCO_3$ crystals around 39.6–44.4 nm, indicating that the resulted aragonite rods and clusters were composed of aggregates of crystals.

The aragonite phase of the sample was further confirmed by Fourier transform infrared spectroscopy (FT-IR) spectrum shown

Table 1
Sythesis conditions and physical properties of the samples.

Sample U of Ref. [22]	$CaCl_2$ (mol dm^{-3})	($CO(NH_2)_2$) (mol dm^{-3})	PVP (g cm^{-3})	Time (h)	Morphology	Aspect ratio
	0.25	0.75	10	3	Needle-like	10
Sample	Synthesis conditions (M)				Morphology	Mean crystallite size, *D* (nm)
	$Ca(CH_3COO)_2$ (M)	($CO(NH_2)_2$) (M)	PVP (mM)	Time (h)		
1#	2.0	4.0	2.5	24	Rod-like	39.64
2#	2.0	6.0	2.5	24	Bundle-like	41.69
3#	2.0	8.0	2.5	24	Bouquet-like, dumbbell-like	44.24
4#	2.0	10.0	2.5	24	Bouquet-like/dumbbell-like	44.44
5#	2.0	6.0	0	24	Rod-like	49.24
6#	2.0	6.0	2.5	24	Bouquet-like, dumbbell	41.69
7#	2.0	6.0	5.0	24	Bouquet-like, dumbbell	41.02
8#	2.0	6.0	7.5	24	Bouquet-like, dumbbell	39.77