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Biomimetic synthesis of aragonite superstructures using hexamethylenetetramine

Long Chen [a,b,c], Fangzhi Huang [a], Shikuo Li [a], Yuhua Shen [a,*], Anjian Xie [a,*], Jian Pan [c], Yaping Zhang [a], Yan Cai [a]

[a] School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, PR China
[b] Department of Chemistry, Huangshan University, Huangshan 245041, PR China
[c] Post-Doctoral Scientific Research Workstation, HuangShan NOVEL Co. Ltd, Huangshan 245061, PR China

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ABSTRACT

In this paper, biomimetic synthesis of aragonite superstructures using a low molecular weight organic-hexamethylenetetramine (HMT) as an additive in the presence of CO_2 supplied by an ammonium carbonate ($(NH_4)_2CO_3$) diffusion method at room temperature was studied. The products were characterized by scanning or transmission electron microscopy, Fourier transform infrared (FT-IR) spectroscopy, X-ray powder diffractometry, and selected area electron diffraction. The results showed the aragonite superstructures especially dumbbell-flower-like ones were obtained. The formation process of calcium carbonate ($CaCO_3$) in HMT aqueous solution was investigated, suggesting that the products transformed from calcite to vaterite primarily, and then changed into a mixture of aragonite and calcite with an increase of reaction time. The formation mechanism of $CaCO_3$ in HMT solution was also discussed, revealing that aragonite might be controlled by HMT molecules and NH_4^+ ions together.

1. Introduction

Calcium carbonate ($CaCO_3$) has attracted considerable attention as it is not only one of the most abundant biomaterials in nature but also an important inorganic material with various industrial applications as filler in paper, rubber, plastics, and paints [1,2]. $CaCO_3$ often occurs as three anhydrous crystalline polymorphs such as calcite, aragonite, and vaterite [3]. Calcite is the most thermodynamically stable form of calcium carbonate under ambient conditions; the other two anhydrous crystalline forms are metastable in nature, with vaterite being particularly unstable [4]. Some biomimetic templates or additives such as Langmuir monolayers,[5] dynamic liquid–liquid interfaces [6], self-assembled monolayers [7], lipid bilayer stacks [8], vesicles [9], proteins extracted from $CaCO_3$-rich organisms [10] or synthetic molecules such as polymers [11,12] have been used for the synthesis of $CaCO_3$. More recently, Zhang et al. prepared $CaCO_3$ particles with different morphologies and polymorphs in the presence of p-aminobenzene sulfonic acid anhydrous-L-Lysine (L-Lys) complexes [13]. We have also synthesized $CaCO_3$ crystals with different morphologies using bacteria [14] and plant [15].

In biomineralization, polymorph selection is a key issue because different polymorphs offer the possibility of different materials properties. Excellent examples of polymorph control are found in organisms such as mollusks, which can selectively deposit aragonite, a specific polymorph of $CaCO_3$, under the control of biopolymers [16]. It has previously been reported that aragonite is formed in the presence of several extracted macromolecules from different shells in the presence [17] or absence [18] of an organic matrix, under compressed monolayers [19,20], at the liquid–liquid interface in a radial Hele–Shaw cell [6], by applying a double hydrophilic block copolymer [21], from the transformation of amorphous calcium carbonate nanoparticles in reverse surfactant microemulsions [22], by heat-induced precipitation onto self-assembled monolayers of anthracene-terminated thiol chains [7], or by high-power ultrasonic irradiation at certain sound amplitudes [23]. Yu et al. synthesized aragonite crystals in ethanol/water solution [24]. Our group obtained aragonite crystals in different Mg^{2+}/amino acid systems [25]. More recently, Gilbert showed that the N16N peptide self-assembled into layers and promoted aragonite growth in lamellar crystals [26].

To our knowledge, aragonite whiskers [27], sheaf bundles [21], fibers [28], tablets/films [29], needles [30], rods or spindles [23], thin-film [31], microspheres [32], etc. have been obtained by researchers. In this paper, the unusual dumbbell-flower-like aragonite superstructures were firstly synthesized using a low molecular weight organic-hexamethylenetetramine (HMT) as a modifier. One molecule

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* Corresponding authors. Fax: +86 551 5108702.
E-mail addresses: s_yuhua@163.com (Y. Shen), anjx@163.com (A. Xie).

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of hexamethylenetetramine has four six-atom loops. We chose the low molecular weight organic HMT with complex structure as a modifier to control the growth of $CaCO_3$ crystals, in order to simulate the biomineralization process. The aragonite crystals obtained may have applications such as using as a filler of functional polymers, etc. In general, the temperature of aragonite formation from a solution is above 40 °C [33]. Here, we found that aragonite superstructures were formed in HMT aqueous solution at room temperature. Very interestingly, the products transformed from calcite to vaterite primarily, and then changed into a mixture of aragonite and calcite with an increase of reaction time. The possible formation mechanism of aragonite in the presence of HMT was discussed. This study is very significant not only for synthesizing new and special functional materials, but also for providing new insights into biomineralization mechanism.

2. Experimental details

2.1. Materials and instruments

Anhydrous calcium chloride ($CaCl_2$), hexamethylenetetramine ($C_6H_{12}N_4$), ammonium carbonate ($(NH_4)_2CO_3$), and anhydrous ethanol were obtained commercially and were also analytically pure. All reagents above were used without further purification. Double-distilled water was used in all the experiments.

Fourier transform infrared spectroscopy (Nicolet 870, America) with a resolution of 4 cm^{-1} and a wave number range from 400 to 4000 cm^{-1} using the KBr pellet technique, X-ray diffractometer (DX-2000, Japan) using Cu$K\alpha$ radiation at a scan rate of 0.06° 2θ S^{-1}, scanning electron microscopy (KYKY-EM3200, China; or Hitachi X-650, Japan) with an accelerating voltage of 18 or 20 kV were utilized to analyze our products. Transmission electron microscopy and selected area electron diffraction of the products were carried out on a JEM model 100SX electron microscope instrument (Japan Electron Co.) operated at an accelerating voltage at 200 kV. A conductivity meter (DDSJ-308, Shanghai, China) was also used.

2.2. Methods

2.2.1. Synthesis of $CaCo_3$ in different concentration of HMT aqueous solutions

First, seven groups of solutions were prepared (shown in Table 1). Then 50 mL of Solution 1 and the same volume of Solution 2 in every group were mixed completely, obtaining seven mixtures (marked as Mixture 1–7 orderly). Four beakers of Mixture 6 (containing 0.05 mol/L HMT and the same concentration of $CaCl_2$) and only one beaker of other mixtures each were prepared. Then above ten beakers containing the seven kinds of mixtures each were covered with PVC film, which was punched with four needle holes and placed in a larger desiccator. A small (50 mL) beaker containing 5.0 g of crushed ammonium carbonate solid was also covered with PVC film, punched with four holes, and placed at the bottom of the desiccator. This desiccator was placed at room temperature (21–24 °C) for 7 days. In addition, when the reaction time reaches to 1, 2.5, and 48 h(s), a beaker containing mixture 6 was taken out for kinetics measurement (the precipitates were characterized).

Table 1
Components of seven groups of reaction solutions.

Groups	Solution 1	Solution 2
1	Distilled water	0.01 mol/L $CaCl_2$
2	0.01 mol/L HMT	
3	0.1 mol/L HMT	
4	Distilled water	0.1 mol/L $CaCl_2$
5	0.02 mol/L HMT	
6	0.1 mol/L HMT	
7	0.5 mol/L HMT	

The white precipitates produced in the above reaction solutions were separated from solutions by centrifugation (centrifugation rate, 4000 rpm), washed three times with double-distilled water and ethanol, and then vacuum dried for further determination.

The sizes and morphologies of the products were examined by scanning electron microscopy (SEM), while their components and crystal types were determined by Fourier transform infrared spectroscopy (FT-IR) and X-ray powder diffractometry (XRD) or selected area electron diffraction (SAED).

2.2.2. Conductivity measurement of $CaCl_2$ solutions before and after adding HMT

Conductivity of different aqueous solutions including 15 mL 0.05 mol/L HMT, 0.01 mol/L $CaCl_2$, and a mixed solution containing 0.05 mol/L HMT and 0.01 mol/L $CaCl_2$ was measured, respectively, for investigating the interaction between HMT molecules and Ca^{2+} ions.

3. Results and discussion

Fig. 1a–f shows the SEM images of $CaCO_3$ particles obtained from 0.005 mol/L $CaCl_2$ aqueous solutions containing different concentration of HMT after 7 days of reaction. From Fig. 1a, it may be seen that most of the particles obtained are rhombohedral without HMT. The enlarged image (Fig. 1b) shows that the particles are slippery with the length of diagonal from about 8 to 10 μm. Fig. 2a shows the FTIR spectrum of the as-prepared $CaCO_3$. Absorption bands centered at 874 and 712 cm^{-1} characteristic of the calcite phase of $CaCO_3$ are seen. The corresponding XRD pattern (Fig. 3a) of the $CaCO_3$ crystals displays the following diffraction peaks (2θ[°]): 23.02°, 29.38°, 31.42°, 35.92°, 39.37°, 43.12°, 47.30°, and 48.49°, which can be correlated to the ($h\,k\,l$) indices (0 1 2), (1 0 4), (0 0 6), (1 1 0), (1 1 3), (2 0 2), (0 2 4), and (1 1 6), of calcite (JCPDS card number 72-1652). This is in agreement with the FTIR result.

When the mixed solution contains 0.005 mol/L HMT, two types of products can be seen (Fig. 1c and d). One is still rhombohedral, the size of which is close to that of those formed without HMT. The other is bunchy constructed from needle-like building units. The length of each "needle" is about 7–10 μm and the diameter of it is tens to hundreds nanometers. The diameter of the bundles is about 1–3 μm. It can be concluded that HMT molecules have an influence on the morphology of the products. The related FTIR spectrum shows that the characteristic peaks of the products are located at 874, 850, and 712 cm^{-1} (Fig. 2b), suggesting they are a mixture of aragonite and calcite. The intensity of the peak 850 cm^{-1} is stronger, implying that the higher content of aragonite in the products. The XRD pattern (Fig. 3b) of the as-prepared $CaCO_3$ crystals obtained displays the following diffraction peaks (2θ[°]): 23.02°, 26.23°, 27.24°, 29.36°, 31.42°, 33.15°, 35.92°, 37.28°, 37.90°, 38.44°, 39.37°, 43.11°, 45.51°, 47.30°, and 48.49°, which can be correlated to the ($h\,k\,l$) indices (0 1 2), (1 0 4), (0 0 6), (1 1 0), (1 1 3), (2 0 2), (0 2 4), (1 1 6), of calcite (JCPDS card number 72-1652), and (1 1 1), (0 2 1), (0 1 2), (0 3 1), (1 1 2), (1 3 0), (0 4 0), of aragonite (JCPDS card number 76-0606). This is also in agreement with the FTIR result.

When the concentration of HMT in the reaction solution increases to 0.05 mol/L, novel dumbbell-flower-like $CaCO_3$ particles except for large portion of rhombohedral ones can be observed