

Transformation of novel morphologies and polymorphs of CaCO₃ crystals induced by the anionic surfactant SDS

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ABSTRACT

Anionic surfactant, sodium dodecyl sulfate (SDS), was used as a template to modify the formation of CaCO₃ crystals. Aragonite was produced when the concentration of SDS was controlled at 0.5 mM. The rod-shaped aragonite aggregated by block-like particles was fabricated. Pure vaterite with a novel flower-shaped morphology was obtained when the concentration of SDS was 1.0 mM. When the concentration of SDS was increased to 2.5 mM, a mixture composed of vaterite and calcite was produced. And the as-prepared sample showed various morphologies, including tube-shaped, rod-shaped and hexagonal structures. However, the most interesting result is that rhombohedral calcite may be transformed from hexagonal vaterite. This result may prove useful to the further investigation of the processes of biomineralization.

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1. Introduction

Biological materials have unique structures and morphologies, which obtain much better performance than that for their constitute natural minerals. Many organisms make use of calcium carbonate as a constituent of their skeleton or as a protective shell, such as in sea shells, snail shells, and bird's eggs. CaCO₃ can crystallize as calcite, aragonite, or vaterite. Calcite and aragonite are the most common biologically formed CaCO₃ polymorphs. Vaterite, as a less stable polymorph, will transform into calcite through a solvent-mediated process [1]. Biomimetic synthesis and polymorph-control of CaCO₃ crystals have been studied in great detail as reviewed by Cölfen [2]. Many investigations have demonstrated that the properties of CaCO₃ crystals, such as the crystal polymorph, the particle size and morphology, are strongly dependent on the preparation methods and additives [3–5]. Water-soluble additives, such as anionic surfactants, have always been selected to modify the polymorph of CaCO₃ [6–11]. In our previous report [12], the anionic surfactant, sodium dodecyl benzene sulfonate (SDBS), was used as a template to modify the forming processes of CaCO₃ crystals, and various polymorphs of CaCO₃ crystals were obtained. However, no effect of SDS on polymorphs of CaCO₃ was found, the formation of calcite from SDS solutions may be attributed to the tridentate motif of oxygen atoms in HSO₃[−] terminated monolayers, favoring the nucleation of the (001) plane of calcite in which carbonate anions are parallel to the plane [8].

In this paper, SDS was employed as a template to control the growth of CaCO₃ crystals at 90 °C. Structures transformations from aragonite to vaterite and calcite were found. Novel morphologies of CaCO₃ crystals were also obtained.

2. Materials and methods

2.1. Materials

All the chemicals, including urea, calcium acetate and anionic surfactant sodium dodecyl sulfate (SDS), purchased from Sinopharm Chemical Reagent Company, were of analytical grade and used as-received without further purification. De-ionized water was used as the solvent.

2.2. Methods

For the experiments, 50 mM Ca(CH₃COO)₂ and 0.25 M CO(NH₂)₂ were put into a Teflon-lined stainless-steel autoclave, together with concentrations of SDS of 0.5, 1.0 or 2.5 mM, respectively. This volume of chemicals was up to 70% of the total volume of the Teflon cylinder (100 ml). The autoclave was maintained at 90 °C for 24 h, and subsequently cooled down to room temperature. The resulting precipitate was washed with water and alcohol several times, and dried at room temperature for more than 24 h in vacuum.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded using a Bruker D8 Advanced XRD diffractometer with Cu K α radiation at a scanning rate of 0.04° s^{−1}. Scanning electron microscope (SEM) images were taken with a Hitachi S4800, fitted with a field emission source, and working at 20 kV. All samples were mounted on copper stubs and sputter coated with gold prior to examination. Selected-area electron diffraction (SAED) was obtained on a 200 kV Hitachi, Model H-800 microscope. Infrared spectroscopic analysis was performed in transmission mode (FT-IR) using a Nicolet Aexus 470, with scanning from 4000 to 500 cm^{−1} by using KBr pellets. The curves of thermogravimetry (TG) were obtained by a NETZSCH STA 409 PC/PG.

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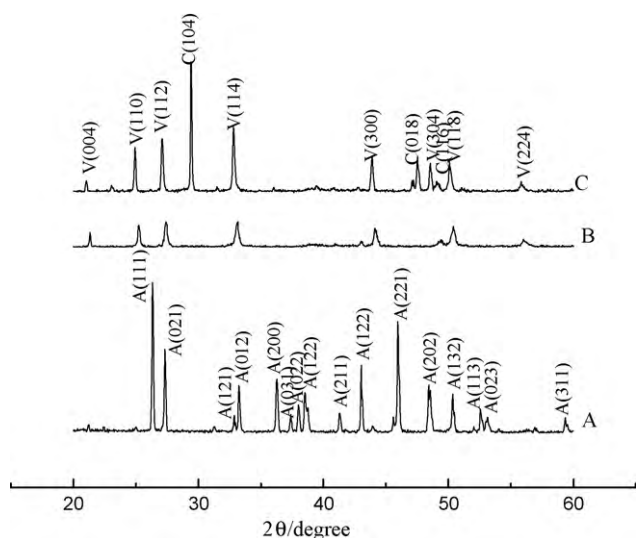


Fig. 1. XRD patterns of the as-obtained samples at 90 °C with different concentrations of SDS solutions: (A) 0.5 mM; (B) 1.0 mM; (C) 2.5 mM.

3. Results and discussion

The XRD patterns of the obtained samples with different concentrations of SDS at 90 °C are given in Fig. 1. In comparison with their standard JCPDS files (aragonite: 5-0453; calcite: 25-0127; vaterite: 33-0268), the Bragg reflections were marked with C, A and V, which correspond to the calcite polymorph, aragonite polymorph and vaterite polymorph, respectively. When the concentration of SDS was 0.5 mM, pure aragonite was fabricated as shown in Fig. 1A. When the concentration of SDS was increased to 1.0 mM, pure vaterite was obtained as given in Fig. 1B. A mixture composed of calcite and vaterite was fabricated when the concentration of SDS was further increased to 2.5 mM, as seen in Fig. 1C. When the concentration of SDS was increased to 10.0 mM, a mixture composed of calcite and vaterite was still fabricated (the result was not shown here). The contents of aragonite, vaterite and calcite contained in the as-prepared samples were calculated according to the reference [13] and are shown in Fig. 2. In order to show the effect of SDS concentration on the polymorph selection of CaCO₃ crystals, the result obtained in our previous report [14] is also given in Fig. 2, for which no SDS was added to the reacting system.

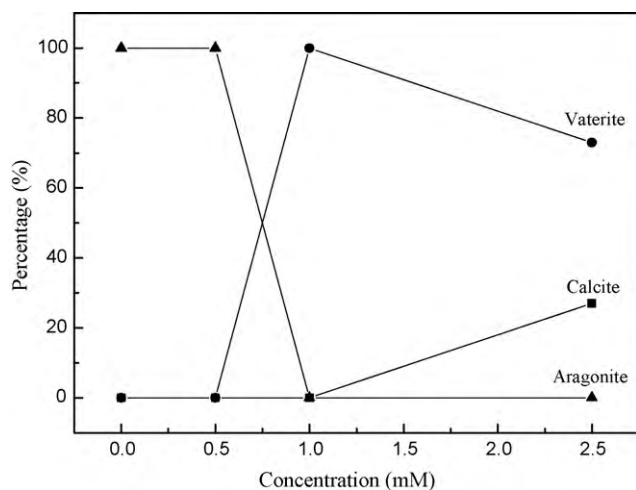


Fig. 2. Percentage of three different crystals of CaCO₃ with different concentrations of SDS solutions. (●) Vaterite, (▲) aragonite, and (■) calcite.

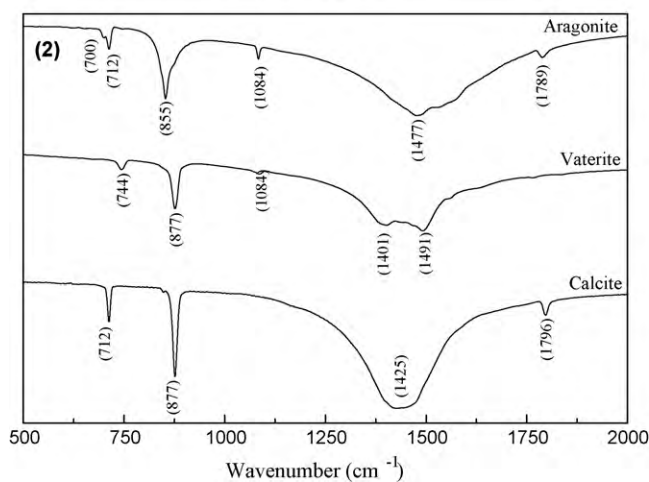
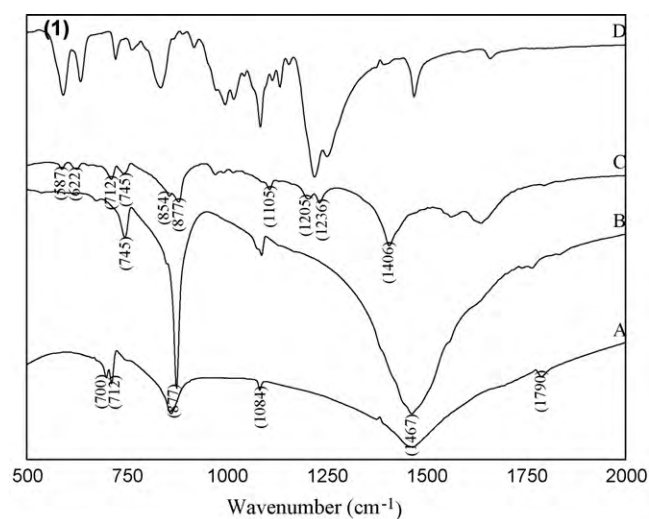


Fig. 3. (1) FT-IR spectra of CaCO₃ crystals obtained with different concentrations of SDS solutions: (A) 0.5 mM; (B) 1.0 mM; (C) 2.5 mM; (D) SDS. (2) FT-IR spectra of pure calcite, vaterite and aragonite.

The results are further demonstrated by FT-IR as given in Fig. 3(1). According to references [15,16], vibrational bands at about 1083 and 854 cm⁻¹ can be assigned to the characteristic symmetric carbonate stretching (ν_1 mode) and a carbonate out-of-plane

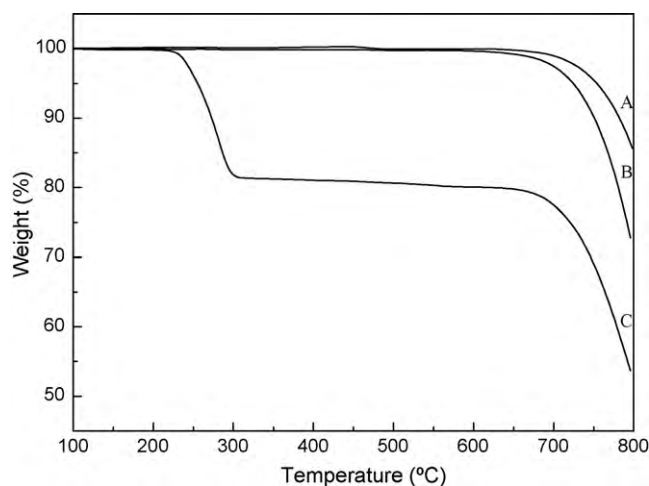


Fig. 4. TG spectra of CaCO₃ obtained with different concentrations of SDS solutions: (A) 0.5 mM; (B) 1.0 mM; (C) 2.5 mM.

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