Fabrication of Calcium Carbonate with Exquisite Morphologies and Colors through a New Controlled Precipitation Approach

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(Received July 2, 2004; CL-040783)

A new approach involving the in situ hydrolysis of diethyl carbonate in calcium-containing solution was proposed for the controlled precipitation of $CaCO_3$. $CaCO_3$ crystals with exquisite morphologies and colors have been fabricated through this approach in the presence of organic molecules.

Calcium carbonate ($CaCO_3$), an important kind of biomineral, widely exists in the lower creatures and exhibits a rich diversity of peculiar morphologies.[1] Controlled precipitation of $CaCO_3$ crystals under mild conditions mimicking the slow mineralization process in nature is critical to the study of the biomineralization process under laboratory conditions. Three approaches have been developed for the controlled precipitation of $CaCO_3$: gas diffusion method,[2] double-jet technique,[3] and Kitano procedure.[4] However, some defects such as low reproducibility,[5] vigorous stir (unlike the static conditions in natural biomineralization), and time-consuming operation still exist in the above approaches. Urea has been used as the in situ CO_3^{2-} source in hydrothermal[6] or solvothermal[7] growth of vaterite (a metastable polymorph of $CaCO_3$). However, the high decomposition temperature of urea in solution (ca. 100 °C) was obviously unacceptable in biological systems, which greatly restricted its application in the study of biomineralization process of $CaCO_3$. Therefore, a simple and controllable approach to fabricate $CaCO_3$ under mild conditions is still desirable.

It has been reported that the interaction between organic biomolecules and $CaCO_3$ crystals is of pivotal importance in controlling the morphology and/or the polymorph of $CaCO_3$ in the natural biomineralization process.[1] Recently, to study such organic–inorganic interaction, various biomacromolecules directly extracted from creatures and synthetic compounds/macromolecules have been added in the biomimetic synthesis of $CaCO_3$.[8] Notably, some organic dyes have been applied in staining $CaCO_3$ crystals to distinguish the different crystalline polymorph of $CaCO_3$.[9] Such experiments implied that organic dyes may also be promising candidates for controlling the crystal morphology and/or polymorph of $CaCO_3$. Herein, we report a facile approach to the controlled precipitation of $CaCO_3$ by in situ hydrolysis of diethyl carbonate in $CaCl_2$ solution under mild conditions, which simulates the slow formation of $CaCO_3$ in nature. Furthermore, when a variety of organic dye molecules were added to the synthetic system, various $CaCO_3$ crystals with unique morphologies and colors were fabricated.

The synthesis procedure was carried out in a glass beaker, which was washed with 1 M HCl and deionized water before experiment. Typically, 0.50 g of ammonia solution (25 wt %) was added to 200 mL of 10 mM $CaCl_2$ solution, and then a certain amount of organic dye (e.g. 0.30 g of eosin Y, C. I. No. 45380[10]) was dissolved in this calcium-containing solution if necessary. Afterward, a glass slide (for microscope use) was placed into the solution as the substrate for $CaCO_3$ growth and 0.24 g of diethyl carbonate was added to the synthetic solution. Finally, the glass beaker was sealed and statically placed in a 25 °C water bath for 18 h. The glass slide covered with $CaCO_3$ crystals was washed with deionized water and dried at room temperature for further characterization.

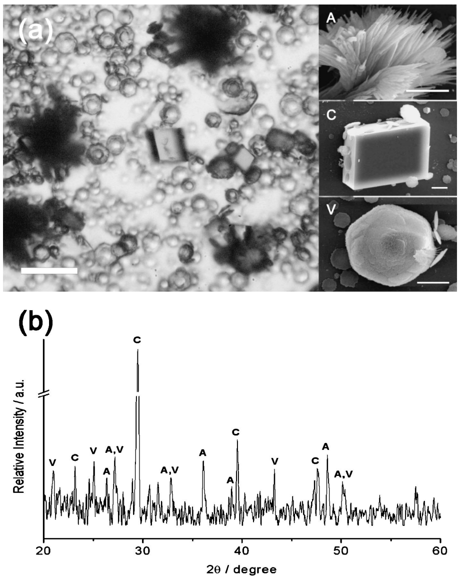

Figure 1. Optical micrograph (a), SEM images (a, insets) and XRD pattern (b) of $CaCO_3$ fabricated in the absence of organic dye molecules. Scale bars in optical micrograph and SEM images are 40 and 4 µm, respectively; Symbols A, C, and V denote aragonite, calcite and vaterite, respectively.

Figure 1a shows the optical micrograph and scanning electron microscope (SEM) images of the $CaCO_3$ product synthesized in the absence of dye molecules. The product comprised hexagonal vaterite discs (composed of nanoparticles), calcite rhombohedra and flower-like aragonites, according to its optical micrograph and X-ray diffraction (XRD) pattern (Figure 1b). Apparently, our approach involving the in situ hydrolysis of diethyl carbonate did not show any discrimination against the three crystalline polymorphs of $CaCO_3$ so that it could be universally applied to fabricate any polymorph of $CaCO_3$ in the presence of controlling agent. On the other hand, owing to the slow generation of CO_3^{2-} through the hydrolysis of diethyl carbonate in the alkaline solution ($pH \approx 10.8$), the observable formation of $CaCO_3$ was retarded to several hours later, which was the premise to achieve a controllable precipitation of $CaCO_3$ in biomimetic synthesis. Because all $CaCO_3$ crystals were tightly attached to the substrate and the synthetic solution was very clear, we

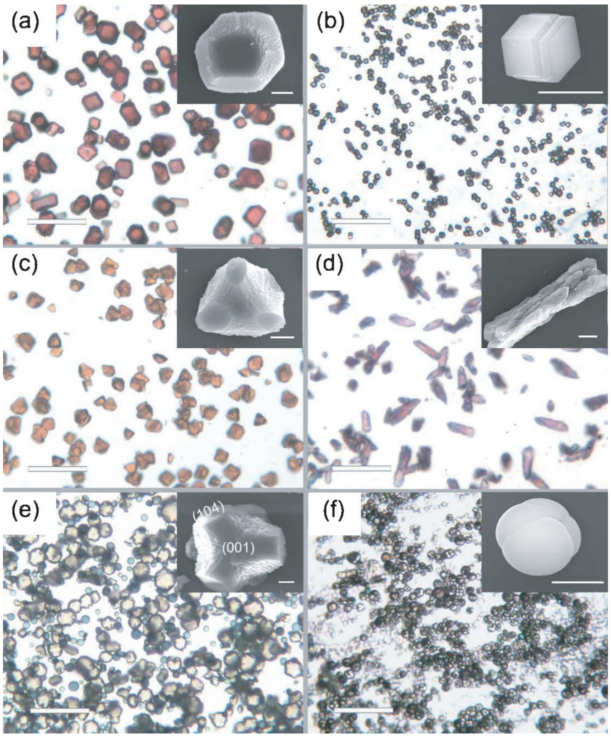

Figure 2. Optical micrographs and SEM images (insets) of $CaCO_3$ fabricated in the presence of organic molecules: (a) $1.50\,g\,L^{-1}$ eosin Y, (b) $1.50\,g\,L^{-1}$ eosin Y (direct mixing of $CaCl_2$ and Na_2CO_3 solutions), (c) $2.00\,g\,L^{-1}$ fluorescein sodium, (d) $0.25\,g\,L^{-1}$ alizarin red S, (e) $0.50\,g\,L^{-1}$ methyl blue, and (f) $1.00\,g\,L^{-1}$ casein. Scale bars in optical micrographs and SEM images are 50 and 4 μm, respectively.

suggested that the nucleation process in our approach was heterogenous, which was preferred in biomimetic synthesis.[11]

Organic dyes have abundant molecular structures and functional groups, which make them promising model compounds for studying the control of crystal morphologies through organic–inorganic interactions.[12] When organic dyes with negatively charged functional groups were introduced to our synthetic system, interestingly, the resulted $CaCO_3$ crystals possessed not only unique polymorph of calcite but also intriguing morphologies and colors. Eosin Y can interact with $CaCO_3$ crystal through its carboxylate and phenolate groups, leading to the formation of hexagonal carmine calcites with stepped crystal faces (Figure 2a), whose 104 face was predominantly expressed according to the XRD pattern (not shown). By comparison, if $CaCl_2$ and Na_2CO_3 solutions were directly mixed in the presence of eosin Y, only calcite rhombohedra (Figure 2b) were obtained and the products were poorly dyed, which clearly proved the controllability of our approach over the growth of $CaCO_3$. When fluorescein sodium (C. I. No. 45350) with only phenolate groups was introduced, triagonal brown calcite crystals with stepped crystal faces (Figure 2c) were induced. Alizarin red S (C.I. No. 58005) with sulphonate group was often adopted to stain calcium-containing biominerals in medical research.[13] Dogbone-like violet calcites (Figure 2d) were obtained by adding alizarin red S to the synthetic solution. Methyl blue (C. I. No. 42780) exhibited higher controllability over the nucleation process of $CaCO_3$. The main product was twinned Y-shaped calcite crystal (Figure 2e), which just resembled the molecular conformation of methyl blue itself. A small amount of spherical or peanut-like crystals was also found in the product. According to the XRD pattern, when the concentration of methyl blue was relatively low (e.g. $0.25\,g\,L^{-1}$), only the 104 diffraction peak of calcite was observed. However, the 006 diffraction peak would be drastically enhanced if the concentration of methyl blue was increased to $1.0\,g\,L^{-1}$. It has been reported that sulfate group can interact with the (001) face of calcite and lead to oriented nucleation.[14] The three sulphonate groups (structurally similar to sulfate group) on a single methyl blue molecule made it strongly interact with the (001) face of calcite and led to the preferential nucleation of calcite parallel to the *c* axis. The colored $CaCO_3$ did not bleach even treated in boiling water for more than 5 h, indicating that the dye molecules were occluded as defects in the $CaCO_3$ crystals during the growth process as biomacromolecules did in natural biomineralization.[15] To verify the validity of diethyl carbonate in the controlled precipitation of $CaCO_3$ with different polymorph, casein, a kind of phosphorylated protein, was employed and cotton-like pure vaterite crystals (Figure 2f) were obtained.

In summary, a novel method was proposed to the controlled precipitation of $CaCO_3$ by using diethyl carbonate as the $CO_3{}^{2-}$ source through in situ hydrolysis under mild conditions. $CaCO_3$ crystals with various morphologies, colors, and polymorphs have been fabricated through this new approach with the aid of organic molecules.

This work is supported by the NSFC (20273016, 20233030, 20325313, 20303003), the SNPC (0249nm028, 03DJ14004) and the Major State Basic Research Development Program (2003CB615807).

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Published on the web (Advance View) August 28, 2004; DOI 10.1246/cl.2004.1248