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# Preparation and Characterization of Biomorphic $CaCO_3$ with Hierarchically Ordered Micro- and Nano-Structures†

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Biomorphic $CaCO_3$ with different hierarchically ordered micro- and nanostructures was fabricated using chitosan solution as soft template. Influences of Ca/Mg molar ratio and temperature on crystalline morphology of $CaCO_3$ were investigated by XRD, FTIR and SEM. The results show that facts including temperature, the ratio of calcium to magnesium have key effect on the morphology evolution of calcium carbonate.

**Key Words: Biomorphic, $CaCO_3$, Nanostructure.**

## INTRODUCTION

Recently, hierarchical inorganic materials possessed good optical and mechanical properties prepared by mimicking natural biomineralization processes have attracted much attention[1]. Calcium carbonate is one of the most abundant minerals in nature. It has three crystalline polymorphs, *i.e.*, vaterite, aragonite and calcite. Among them, calcite is the most stable polymorph thermodynamically and often found in biominerals[2]. Meanwhile, it is known that the organic matrix plays an important role in mineralization for mediating the inorganic structure, morphology and polymorphs. Many bioactive materials have been widely chosen to control the phase and morphology of calcium carbonate to form laminated structures, including Langmuir monolayer, self-assembled films, double-hydrophilic block copolymers, macromolecules and so on. As one of the most important bioactive molecules, chitosan has been employed to induce the nucleation of calcium carbonate widely, but its role on biomineralization is still needed to be understood[3]. In this article, calcium carbonate particles were prepared by the method of gas diffusion using chitosan solution as organic soft template and $Mg^{2+}$ as molecule additives. Effects of the different Ca/Mg molar ratio and temperature on crystalline morphology of calcium carbonates were studied.

## EXPERIMENTAL

The transparent chitosan acetic acid solution was firstly prepared by stirring 1 g chitosan with 100 mL acetic acid at room temperature for 2 h. Secondly, 0.5550 g $CaCl_2$ and 1.0165 g $MgCl_2·6H_2O$ were added into a beaker with a certain amount of double-distilled water under stirring. 100 mL chitosan acetic acid solution was then introduced. The concentrations of $Ca^{2+}$ and $Mg^{2+}$ ions were 0.05 M, respectively. Correspondingly, the solution with $Ca^{2+}/Mg^{2+}$ molar ratio1:2, 1:4, 1:8 were prepared as described above. After that, the beakers covered with parafilm punched with three holes were put into a closed desiccator where a small beaker containing $(NH_4)_2CO_3$ had been placed in advance. Remarkably,the beaker containing $(NH_4)_2CO_3$ was also covered with parafilm, punched with three holes to control the rate of diffusion. Finally, $CO_2$ vapour was diffused into the mixed solutions at different temperature for a given time, a white product was gradually produced. The obtained products were collected, washed with deionized water several times and dried at 60 ºC in air.

## RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the product prepared from the system containing 0.4 mL of chitosan soulution at 25 ºC. The diffraction peaks in Fig. 1(A) at 29.4, 31.4, 47.5 and 61.0º are ascribed to the hkl indices (104), (006), (018) and (208), respectively, which can be indexed as calcite hexagonal $CaCO_3$ form when compares with the JCPDS card files No: 72-1652. In Fig. 1(B), the XRD patterns of $CaCO_3$ prepared in presence of magnesium ion shows only aragonite phase.

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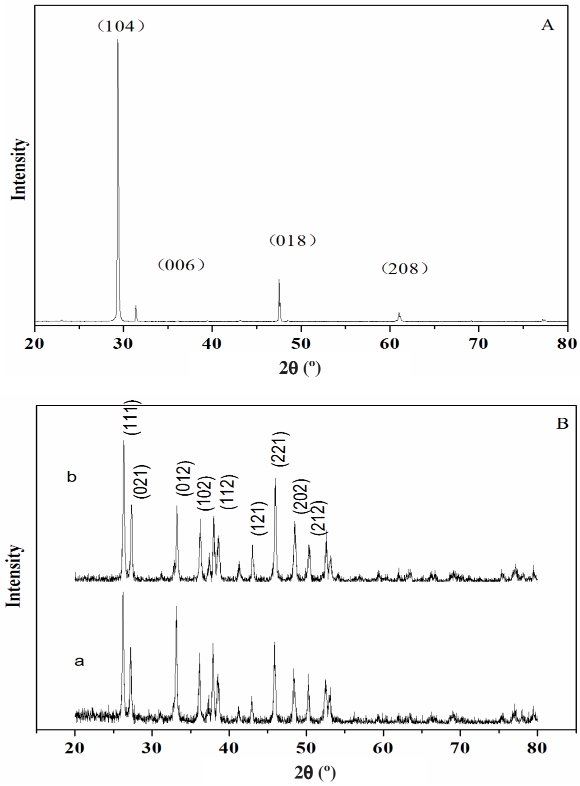

Fig. 1. XRD patterns of products

The formation of product was further confirmed by the energy dispersive spectrum analysis (Fig. 2), from which Ca, Mg, C and O peaks could be clearly found. Furthermore, it can be speculated that the products with distinctive structure is calcium carbonate in which magnesium ion partly entered.

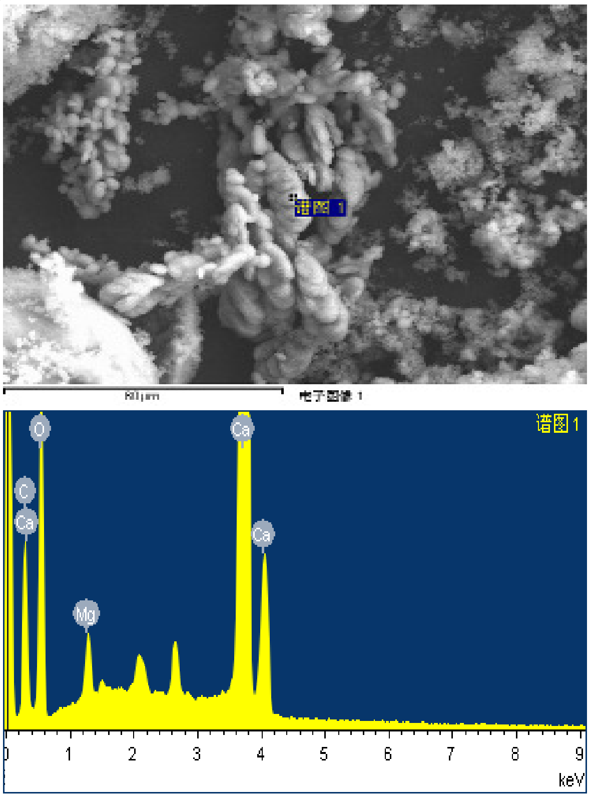

Fig. 2. EDS analysis of $CaCO_3$ prepared of with chitosan and magnesium ion at 10 °C

Fig. 3 shows FT-IR spectra of $CaCO_3$ obtained in chitosan system with different Mg/Ca ratio at 25 °C and the concentration of $Ca^{2+}$ is controlled at 0.05 M. The chitosan shows the peak of -OH stretching vibration at 3400 $cm^{-1}$, while calcium carbonate-chitosan hybrids shift the peak to around 3437$cm^{-1}$. It can be seen that the location of peak move to high frenquency by 37 $cm^{-1}$ so there might be coordination interaction between calcium ion and -OH group of chitosan. Besides, the peak at 1085 $cm^{-1}$ is assigned to the symmetric C-O stretching vibration and it is also characteristic of $CaCO_3$. The peak at 1085 $cm^{-1}$ is assigned to the symmetric C-O stretching vibration and it is also characteristic of $CaCO_3$. The presence of peak at 2516 $cm^{-1}$ and 1788 $cm^{-1}$ is C-H stretching vibration. All of these suggest that chitosan can induce the growth of calcium carbonate. The peaks located at 853 $cm^{-1}$ and 705 $cm^{-1}$ correspond to the out-of-plane blending and in-plane blending modes of $CO_3^{2-}$, respectively and these can be assigned to the characteristic peaks for aragonite[4]. It suggests that the aragonite crystalline form of $CaCO_3$ does not change with increasing Mg/Ca ratio in the presence of chitosan.

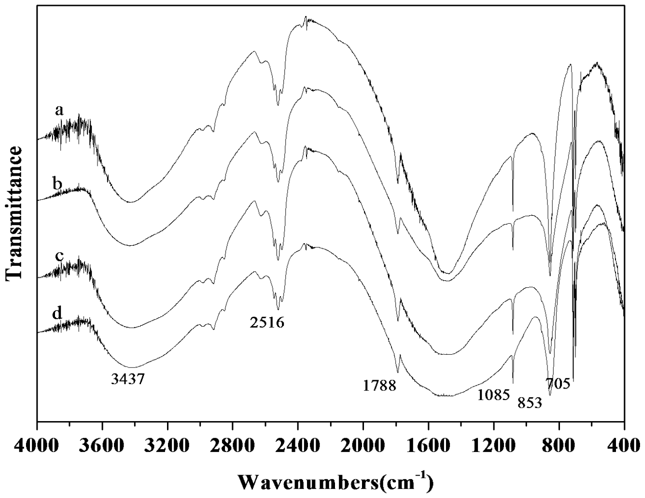

Fig. 3. FT-IR spectrum of $CaCO_3$ obtained in chitosan system with different Mg/Ca ratio: (a) 1:1, (b) 2:1, (c) 4:1, (d) 8:1 with chitosan and magnesium ion at 10 °C

Fig. 4 shows the scanning electron microscopy (SEM) images of the obtained products synthesized from the system containing chitosan solution (0.4 mL, 10 g/L) and different concentration of magnesium ion. With increasing Ca/Mg ratio, the morphology of obtained $CaCO_3$ changed (Figs. 4a-e). In presence of chitosan solution alone, some micron-sized calcium carbonate particles with cube structure were obtained (Fig. 4a). It is known that without additives, the morphology of calcium carbonate is cube. It is therefore suggested that chitosan has little effects on the morphology of calcium carbonate. When magnesium ion was introduced into this system, the morphology of calcium carbonate changed remarkably. They firstly manifest walnut structure, followed as ball-shaped morphology, finally changed into homogeneous dumbbell-like structure (Figs. 4b-e). Interestingly, high-magnification SEM observations showed that these ball-shaped $CaCO_3$ superstructures were comprised of abundant nanparticles *via* self-assembly (lower right corner of Fig. 4d). The ball-shaped $CaCO_3$ was micro-sized with mean diameter of -200 um and its surface was full of macroporous. When the crystallization temperature was settled at 10 ºC and Mg/Ca ratio is up to 8, the crystal clusters display stack-like structure (Fig. 4f), which indicates that the temperature is a key factor on the morphology of products[5].

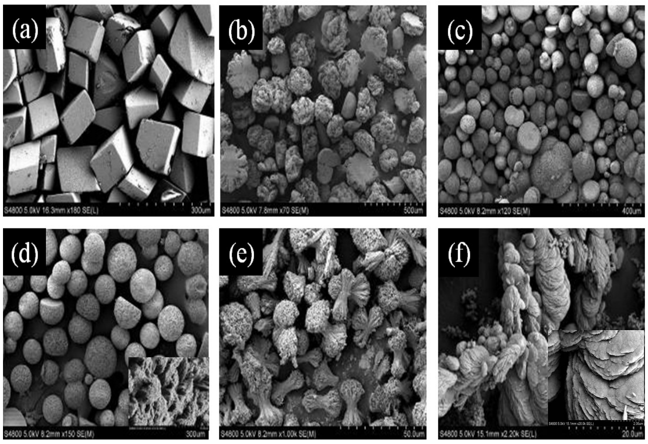

Fig. 4. SEM image of $CaCO_3$ products in presence of chitosan with different Ca/Mg ratio: (a)-(e) 1:0, 1:1, 1:2, 1:4 and 1:8, respectively, at 25 ºC; (f) 1:8 at 10 ºC

## Conclusion

Biomorphic calcium carbonate particles with hierarchically ordered microstructures were fabricated from the system containing chitosan and magnesium ion. With increasing Ca/Mg molar ratio, the morphology of $CaCO_3$ changed significantly. Calcium carbonate crystal with unusual stack-like structure was prepared at 10 ºC when the Mg/Ca molar ratio is up to 8. It was the first time to synthesize $CaCO_3$ with such structure in this system. Besides, the surface of the prepared $CaCO_3$ was bestowed with macroporous.

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