

Assembly Synthesis of Sheet-like Calcite Array and Stable-Vaterite by Supported Liquid Membrane

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Sheet-like calcite array and stable vaterite were synthesized by bio-mimetic supported liquid membrane system under different reaction conditions. Both of the FTIR spectra of products showed narrower peak at 1418 cm^{-1} than that of bulk CaCO_3 , and that of vaterite has a split in this peak.

Keywords calcite, sheet-like, vaterite, supported liquid membrane

Introduction

CaCO_3 can crystallize as calcite, aragonite and vaterite. Calcite and aragonite are the most common biologically formed CaCO_3 polymorphs, and vaterite is transformed into calcite via a solvent mediated process.¹ Calcium carbonate makes an attractive model mineral for studies, since the morphology of CaCO_3 has been the subject to control in biomineralization processes.² And control of vaterite also has significance for various purposes because it has some features such as high specific surface area, high solubility, high dispersion, and small specific gravity compared with the other two crystal phases.³ Therefore the polymorph and morphology control of CaCO_3 has been intensively investigated in recent years.⁴ Double-hydrophilic block copolymers,⁵ the protein macromolecules⁶ and Au nano-colloids have been used as additives for the crystallization of CaCO_3 . In addition, Langmuir monolayer,⁷ foam lamellae,⁸ polymer substrates⁹ and crystal-imprinted polymer surfaces¹⁰ have been used as templates for the polymorph and morphology control of CaCO_3 crystals. However, there was no research simulating the transport way of bio-membrane to control the morphology of CaCO_3 , and furthermore assembled sheet-like calcite array has not been reported. Here we described a novel biomimetic strategy for the assembling synthesis of sheet-like calcite array and stable vaterite by supported liquid membrane (SLM) containing mobile carrier with different concentration.

Experimental

In a typical procedure, 0.2 g of *o*-phenanthroline (phen) was added into 80 mL of chloroform under vigorous stirring at 3000 r/min for 15 min to make an oil

phase. Then the dried polymer membrane was immersed into the oil phase for 20 h. The obtained membrane was treated with filter paper to eliminate remnant oil on surface. 80 mL of CaCl_2 solution and 80 mL of Na_2CO_3 solution were separated by prepared membrane to establish an SLM system. After an appropriate period, the precipitates in Na_2CO_3 solution were separated by centrifuge, and washed by distilled water, acetone and ethanol in sequence. The final products were soaked in ethanol. The structure and morphology of the products were characterized by SEM. FT-IR was used to examine the difference between as-prepared products and bulk CaCO_3 .

Results and discussion

The Figure 1A shows that the calcite prepared by SLM is sheet-like array, and the thickness of a sheet is about 50 nm. Figure 1B shows rhombohedron prepared by direct precipitation in usual solution. The morphology of B is calcite. It is considered that the crystals will adhere to membrane wall naturally for decreasing its surface energy. The membrane itself has surface strength, so it will yield an oriented trend during the process of crystal growth, and at the same time, the crystal growth will be limited by the quantity of Ca^{2+} carried by phen. Therefore calcite grew into sheet-like structure. Furthermore, SLM system has a template effect. It promoted the sheet-like calcite to be assembled to sheet-like array.

Figure 2 shows that the morphology of vaterite is spherical, and the spheres are well dispersed with an average diameter of about 1 μm . The supersaturated solution of CaCO_3 is beneficial for the growth and stabilization of vaterite.¹¹ So the concentration of phen was increased to $0.05\text{ mol}\cdot\text{L}^{-1}$. As a result, Ca^{2+}

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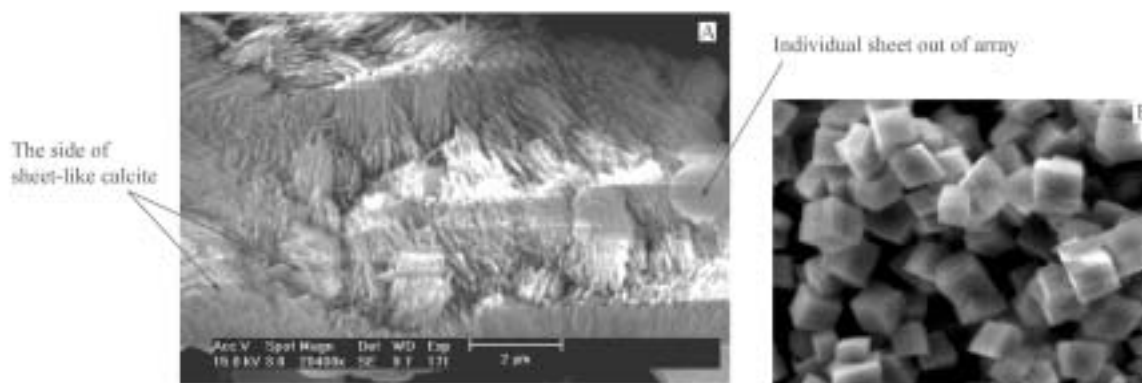


Figure 1 SEM images of calcite obtained by different conditions. A, prepared by SLM containing $0.015 \text{ mol}\cdot\text{L}^{-1}$ phen; B, typical morphology of calcite.

concentration carried by phen was greatly increased in a unit time. Consequently the CaCO_3 critical nucleation concentration was increased and the solution became supersaturated solution. According to the Ostwald rule of stages,¹² metastable vaterite was nucleated and stabilized in supersaturation.

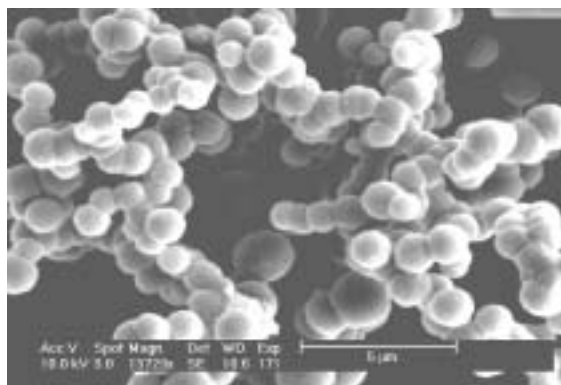


Figure 2 SEM image of vaterite obtained by SLM containing $0.05 \text{ mol}\cdot\text{L}^{-1}$ phen.

It is well known that different crystal form of CaCO_3 shows different absorption band in FTIR spectrum.⁸ The characteristic absorption peaks of vaterite (Figure 3C) are at 877 and 744 cm^{-1} , and those of calcite are at 876 and 713 cm^{-1} (Figures 3A and 3B). The reference bands observed at 714 , 874 , 1418 cm^{-1} can be assigned to the in-plane bending (ν_4), out-of-plane bending (ν_2) and asymmetric stretching (ν_3) modes of CO_3^{2-} , respectively.¹³ As Figure 3 shows B and C have some special performance compared to reference CaCO_3 . Firstly, curve C has a split at 1418 cm^{-1} . Leeuw *et al.*¹⁴ has reported that the structure of vaterite has considerable disorder of the carbonate group leading to partial occupancies of different carbonate sites. For this reason, it can be believed that the inequality of three C—O bonds in vaterite compared with that of calcite should response for the split. Secondly, the peak shape at the band of 1418 cm^{-1} in curves B and C became narrower compared with that in curve A. Earlier studies have reported that the narrow peak shape was due to the quantum size effect, distortion of crystal lattice¹⁵ and abnormal prop-

erty of nano-assembled sphere.^{16,17} It was considered that calcite and vaterite prepared by SLM were assembled by nano-sheet and nano-particles.

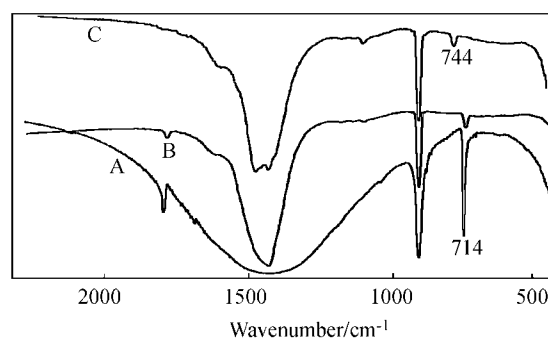


Figure 3 FTIR spectra of CaCO_3 . A, reference bulk calcite; B, calcite prepared by SLM; C, vaterite prepared by SLM.

Conclusion

In summary, sheet-like calcite array and vaterite were synthesized by SLM. Their FTIR spectra have some special features compared to those of bulk CaCO_3 , which was supposed to relate to their nano-microstructure. It can be believed that the SLM method and its products have scientific value for morphology research and nano-device assembly.

References

- 1 Lopezmacipe, A.; Fomezmorales, J.; Rodriguezclemente, R. *J. Cryst. Growth* **1996**, *166*, 1015.
- 2 (a) Lowenstam, H. A. *Science* **1981**, *211*, 1126.
(b) Mann, S. *Nature* **1988**, *332*, 119.
- 3 Naka, K.; Tanaka, Y.; Chujo, Y. *Langmuir* **2002**, *18*, 3655.
- 4 Cölfen, H. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 23
- 5 Sedlak, M.; Antonietti, M.; Cölfen, H. *Macromol. Chem. Phys.* **1998**, *199*, 247.
- 6 Belcher, A. M.; Wu, X. H.; Christensen, R. J.; Hansma, P. K.; Stucky, G. D.; Morse, D. E. *Nature* **1996**, *381*, 36.
- 7 Litvin, A. L.; Valiyaveettil, S.; Kaplan, D. L.; Mann, S. *Adv. Mater.* **1997**, *9*, 124.
- 8 Chen, B. D.; Cilliers, J. J.; Davey, R. J.; Garside, J.; Wood-

- burn, E. T. *J. Am. Chem. Soc.* **1998**, *120*, 1625.
- 9 Dalas, E.; Klepetsanis, P.; Koutsoukos, P. G. *Langmuir* **1999**, *15*, 8322.
- 10 D'Souza, S. M.; Alexander, C.; Carr, S. W.; Waller, A. M.; Whitcombe, M. J.; Vulfson, E. N. *Nature* **1999**, *398*, 312.
- 11 Spanos, N.; Koutsoukos, P. G.; Koutsoukos, P. G. *J. Phys. Chem. B* **1998**, *102*, 6679.
- 12 Ostwald, W. Z. *Phys. Chem.* **1819**, *9*, 289.
- 13 White, W. B. In *Infrared Spectra of Minerals*, Ed.: Farmer, V. C., Mineralogical Society, London, **1974**, pp. 227—284.
- 14 de Leeuw, N. H.; Parker, S. C. *J. Phys. Chem. B.* **1998**, *102*, 2914.
- 15 Shui, M.; Yue, L.; Liu, Q.; Xu, Z. D.; Zheng, Y. F.; Ding, C. H. *Chin. J. Inorg. Chem.* **1999**, *15*, 715 (in Chinese).
- 16 Peng, Q.; Dong, Y. J.; Li, Y. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 3027.
- 17 Wu, Q. S.; Liu, J. K.; Ding, Y. P.; Liu, Q. *Acta Chim. Sinica* **2003**, *61*, 1824 (in Chinese).

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