

Formation of Rod-Shaped Calcite Crystals by Microemulsion-Based Synthesis

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Novel rod-shaped calcite crystals are formed by precipitation from cetyltrimethylammonium bromide (CTAB)/1-pentanol/cyclohexane microemulsions containing calcium chloride and ammonium carbonate. The calcium carbonate initially precipitates as hexagon-shaped vaterite crystals. The vaterite crystals transform to unusual rod-shaped calcite crystals over several days. The rod-shaped calcite crystals are prismatic, with the longest crystal axis displaying (110) crystal faces. A possible mechanism of crystal growth is discussed. The elongated shape of the crystals facilitates the assembly into hierarchical structures and can allow the crystals to be used as templates for fabricating advanced materials.

Calcium carbonate (CaCO_3), one of the most abundant biominerals, exists in three main crystal structures: aragonite, calcite, and vaterite. These crystals have a wide range of naturally occurring crystal habits and are often found assembled into hierarchical structures that result in a variety of intriguing properties in organisms.¹ For example, aragonite crystals assembled in nacreous layers in mollusks show a 3000 times higher hardness than that of synthetic aragonite.² Calcite crystals oriented in the skeletal elements of brittlestars function as microlenses to guide and focus the light on nerve bundles.³ These unique properties are closely related to the natural biomineralization processes, during which the nucleation and growth of CaCO_3 are controlled by proteins or other macromolecules present in organisms.⁴ Inspired by these results, scientists have attempted to create CaCO_3 crystals with various morphologies and properties outside of biological organisms by mimicking the biomineralization processes. Two principle approaches have been developed: the first is the addition of water-soluble additives such as simple metal ions,^{5,6} polymers,^{7,8} and biomolecules^{1,9} to mediate CaCO_3 crystallization and growth through specific interactions between faces of the growing crystals and the additives; the second technique is crystallization within templates including shape-persistent rigid polymers,¹⁰ pliable monolayers of molecular ribbons,¹¹ polycarbonate membranes with cylindrical pores,¹² or less rigid organic gels to form a gelatin matrix.¹³ Confinement of crystallization within templates results in crystals with morphologies modeling that of the template.

Aqueous crystallization and precipitation reactions can be confined within water-in-oil (W/O) microemulsions that consist of nanometer-scale water droplets surrounded by surfactant and dispersed in oil. Microemulsions are thermodynamically stable and spontaneously self-assemble into well-defined structures. The W/O microemulsion can act as a “soft template” and have a profound effect on crystallization and precipitation processes.¹⁴ When crystallization reactions are carried out in microemulsions, the resulting mesoscale crystal surface structure and intrinsic morphology can be simultaneously controlled or directed by the confinement of reagents in the aqueous droplets and adsorption of surface-active agents on the growing crystals. Several attempts to grow CaCO_3 crystals in W/O microemulsions have been conducted recently. For example, in water/sodium dodecyl sulfate/cyclohexane microemulsions, CaCO_3 predominantly formed spherical vaterite instead of the mixture of rhombohedral calcite and round vaterite that forms from the pure aqueous solution.¹⁵ The anionic surfactant lowers local pH and increases supersaturation near the surfactant and water interface through ionic interaction with inorganic cations, altering the preferred structure from calcite to vaterite. CaCO_3 also formed as vaterite when synthesized in oil-rich microemulsions formed with the anionic surfactant sodium bis-2-ethylhexyl-sulfosuccinate, but the crystal structure was surprisingly altered to aragonite with a “nanofilament” morphology as the water content in the microemulsion was increased.¹⁶ CaCO_3 was shown to grow as elongated “superstructures” consisting of stacks of platelike calcite crystals when synthesized in a mixed surfactant microemulsion at high pH.¹⁷ In water/poly(oxyethylene) (1,1,3,3-tetramethylbutyl)phenyl ether/cyclohexane microemulsions, CaCO_3 grew into nanowires 5–30 nm in diameter and more than 10 μm in length.¹⁸ Transmission electron microscopy (TEM) data shows that the CaCO_3 nanowires formed first as nanoparticles through controlled crystallization in aqueous phase, and, subsequently, the surfactant aided the one-dimensional aggregation of nanoparticles and conversion to nanowires, although the crystal structure of the nanowires was not reported.¹⁸ By precipitation from water/cetyltrimethylammonium bromide (CTAB)/*n*-butanol/

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- (1) Meldrum, F. C. *Int. Mater. Rev.* **2003**, *48*, 187.
- (2) Currey, J. D. *Proc. R. Soc. London, Ser. B* **1977**, *196*, 443.
- (3) Aizenberg, J.; Weiner, A. T. S.; Addadi, L.; Hendler, G. *Nature* **2001**, *412*, 819.
- (4) Mann, S.; Archibald, D. D.; Didymus, J. M.; Douglas, T.; Heywood, B. R.; Meldrum, F. C.; Reeves, N. J. *Science* **1993**, *261*, 1286.
- (5) Raz, S.; Weiner, S.; Addadi, L. *Adv. Mater.* **2000**, *12*, 38.
- (6) Pastero, L.; Costa, E.; Bruno, M.; Rubbo, M.; Sgualdino, G.; Aquilano, D. *Cryst. Growth Des.* **2004**, *4*, 485.
- (7) Cölfen, H.; Qi, L. M. *Chem.—Eur. J.* **2001**, *7*, 106.
- (8) Yu, S. H.; Cölfen, H. *J. Mater. Chem.* **2004**, *14*, 2124.
- (9) Orme, C. A.; Noy, A.; Wierzbicki, A.; McBride, M. T.; Grantham, M.; Teng, H. H.; Dove, P. M.; DeYoreo, J. J. *Nature* **2001**, *411*, 775.
- (10) Donners, J. J. M.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *J. Am. Chem. Soc.* **2002**, *124*, 9700.
- (11) Champ, S.; Dickinson, J. A.; Fallon, P. S.; Heywood, B. R.; Mascal, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2716.
- (12) Lose, E.; Meldrum, F. C. *Chem. Commun.* **2001**, 901.
- (13) Grassmann, O.; Müller, G.; Löbmann, P. *Chem. Mater.* **2002**, *14*, 4530.

- (14) Pileni, M. P. *Langmuir* **2001**, *17*, 7476.
- (15) Kang, S. H.; Hirasawa, I.; Kim, W. S.; Choi, C. K. *J. Colloid Interface Sci.* **2005**, *288*, 496.
- (16) Li, M.; Lebeau, B.; Mann, S. *Adv. Mater.* **2003**, *15*, 2032.
- (17) Viravaidya, C.; Li, M.; Mann, S. *Chem. Commun.* **2004**, 2182.
- (18) Kuang, D.; Xu, A. W.; Fang, Y. P.; Ou, H. D.; Liu, H. Q. *J. Cryst. Growth* **2002**, *244*, 379.

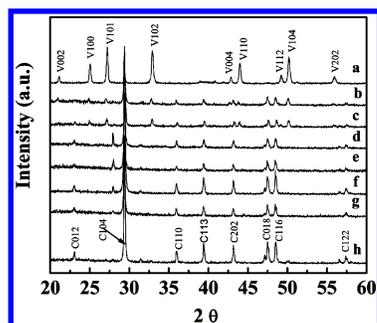


Figure 1. XRD patterns showing transformation of vaterite to calcite in CTAB/1-pentanol/cyclohexane mixtures after (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 8, and (h) 10 days.

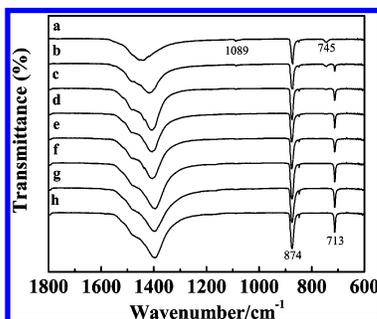


Figure 2. FTIR transmission spectra showing transformation of vaterite to calcite in CTAB/1-pentanol/cyclohexane mixtures after (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 8, and (h) 10 days.

hexadecane microemulsions, 2 μm spherical and rhombohedral (with an aspect ratio near 1) calcite particles were obtained, with

the crystal morphology dependent on the microemulsion composition.¹⁹

Here we report the crystallization of CaCO_3 through precipitation from oil-rich water/CTAB/1-pentanol/cyclohexane microemulsions. Oil-rich microemulsion compositions were chosen to confine crystal nucleation in small W/O droplets, and a cationic surfactant (CTAB) was chosen because it is expected to have strong interaction with the anionic surfaces of CaCO_3 crystals.²⁰ The reactions were carried out for longer times (up to 10 days) than typically investigated in the microemulsion-based synthesis of CaCO_3 to observe crystal transformation into the thermodynamically preferred structure. In a typical synthesis, a microemulsion is formed containing 1 g of CTAB, 30 mL of cyclohexane, 1.5 mL of 1-pentanol, and 1.341 g of CaCl_2 (1.94 M) in aqueous solution. Aqueous $(\text{NH}_4)_2\text{CO}_3$ solution (1.298 g) with the same molar concentration as that of CaCl_2 is then added to the microemulsion under mild magnetic stirring. Upon adding the ammonium carbonate, the microemulsion slowly changes from visually transparent to opaque. After 30 min, a white precipitate is observed at the bottom of the flask when stirring is stopped. The mixture is then maintained at room temperature for up to 10 days without stirring, with a small quantity being removed during this period for observing crystal growth behavior.

Powder X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were employed to study crystal polymorphs. The results are shown in Figures 1 and 2, respectively. In Figure 1, all peaks of the XRD spectra are consistent with the vaterite crystal structure when the reaction was carried out for 1 day. After 2 days, some new peaks appear that are consistent with the calcite crystal structure. As the reaction time is increased, the intensity of the vaterite peaks decreases with time, while the

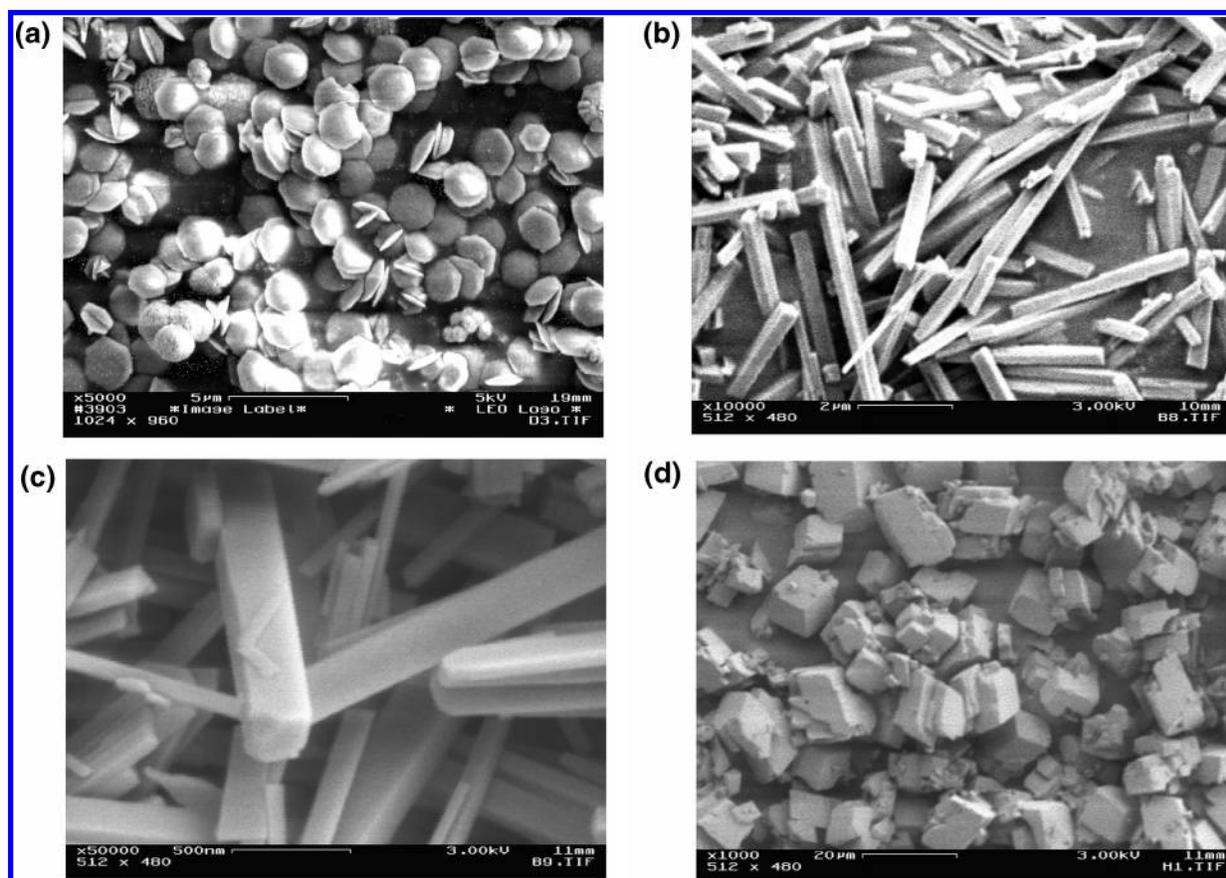


Figure 3. SEM images of calcium carbonate crystals synthesized in W/O microemulsions: (a) hexagonal vaterite crystals after 1 day and (b) novel rod-shaped prismatic calcite crystals after 6 days. A higher magnification image of the prismatic calcite crystals is shown in panel c. For comparison, panel d shows the rhombohedral calcite crystals that form after 6 days in the aqueous solution without the microemulsion.

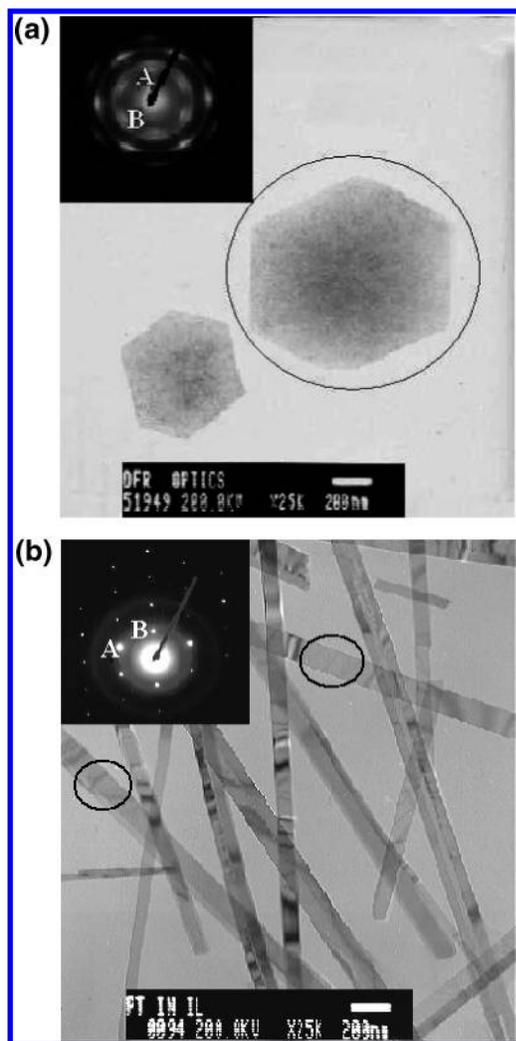


Figure 4. TEM images and corresponding SAED patterns of (a) the hexagonal vaterite formed after 1 day and (b) prismatic calcite produced after 6 days. The SAED patterns were confirmed to be the (a) [001] (reflections: A, (010); B, (100 11210) and (b) [110] (reflections: A, (006); B, (104)) zones of vaterite and calcite, respectively.

intensity of the calcite peaks increases with time, demonstrating calcite formation at the expense of vaterite crystals. After about 4 days, the material appears to be exclusively calcite. Powder XRD indicates that a vaterite-to-calcite transformation occurs and is completed after about 4 days. FTIR spectra further confirmed the XRD analysis of the vaterite-to-calcite transformation. Figure 2 illustrates the characteristic transmittance peaks centered around $745(\nu_4)$, $874(\nu_2)$, and $1089(\nu_1)$ cm^{-1} corresponding to the in-plane bending, out-of-plane bending, and symmetric stretching vibration modes of CO_3^{2-} in vaterite, respectively.²¹ For calcite, ν_1 is only Raman active and ν_4 shifts to 713 cm^{-1} , although the ν_2 position is similar with that of vaterite. The vanishing of ν_1 and emerging of ν_4 of calcite with time is consistent with the decomposition of vaterite and formation of calcite.

The CaCO_3 morphologies were observed with scanning electron microscopy (SEM) and TEM, as presented in Figures 3 and 4. Figure 3a reveals that the precipitates consist of hexagonal vaterite crystals with a small amount of spherical vaterite in the

early growth stage (1 day). After 6 days, every particle appears as prismatic calcite with well-defined faces (Figure 3b). The facets of the prismatic crystals are easily discernible in the image in Figure 3c, which has a higher magnification. The TEM images, Figure 4a,b, demonstrate the same results as those from the SEM observation. Selected area electron diffraction (SAED) patterns are shown as insets in the TEM figures. The circles on the TEM images indicate areas from which the SAED patterns were taken to investigate the CaCO_3 crystal structure. The SAED pattern of particles that have hexagonal shape exhibits bright spots with superimposed arced reflections corresponding to the [001] zone of vaterite single crystals when viewed predominantly top-down. SAED on the prism-shaped crystals always shows the same single-crystal pattern, consistent with the [110] zone of calcite, when recorded from the side of the crystal having the longest axis (such as the circled regions in TEM images).

During the transformation of vaterite to calcite, the microemulsion plays an important role. Control experiments show that CaCO_3 prepared from aqueous solution in the absence of the microemulsion grows into the classical rhombohedral calcite with an aspect ratio around 1, as shown in Figure 3d. It is known that vaterite is the typical metastable crystallization product of CaCO_3 .²² However, the formation of vaterite with hexagonal symmetry is uncommon and usually requires a well-defined condition, such as slow vapor diffusion through the thermal decomposition of ammonium carbonate²² or crystallization in the presence of compressed Langmuir monolayers of octadecylamine.²³ We hypothesize that the microemulsion can regulate hexagonal vaterite growth by confinement and surfactant adsorption, mediating crystal growth kinetics and lowering the free energy of the exposed crystal faces. As shown above, vaterite crystals synthesized in a W/O microemulsion expose (001) faces. The (001) faces are highly polar with high surface free energy.²⁴ Expression of such high-energy faces suggests that some component of the microemulsion is preferentially adsorbing on the (001) faces to lower the surface free energy and stabilize the hexagonal vaterite crystals. One possible explanation is that the interaction between the positively charged CTAB surfactant and the negatively charged (001) faces results in the crystallization of hexagonal vaterite. A previous report has shown that cationic ammonium ions affect the crystallization of CaCO_3 , resulting in hexagonal vaterite with a morphology similar to that shown in Figure 3a.²² Considering the large quantity of CTAB present in our system, it is likely that the cationic surfactant functions in a way similar to that of ammonium and is the key factor controlling hexagonal vaterite crystal growth.

Because of the higher solubility of vaterite, it is usually transformed into the thermodynamically more stable calcite with rhombohedral morphology with exposed lowest energy (104) faces after several days.²² In our experiment, however, the vaterite converts into calcite with unusual prismatic morphology and expressed (110) faces. The formation of such unique morphology is also related to the presence of the microemulsion and the cationic surfactant in the microemulsion, since the control experiment without the microemulsion results in typical rhombohedral calcite (Figure 3d). The vaterite-to-calcite transformation occurs by a dissolution reprecipitation mechanism.²² In this process, the surfactant may function dually as a template to direct calcite growth through structural matching factors and the surface active species to stabilize the formed crystals. The positively

(19) Rock, M. L.; Tranchitella, L. J.; Pilato, R. S. *Colloid Polym. Sci.* **1997**, *275*, 893.

(20) Moulin, P.; Roques, H. J. *Colloid Interface Sci.* **2003**, *261*, 115.

(21) Chakrabarty, D.; Mahapatra, S. J. *Mater. Chem.* **1999**, *9*, 2953.

(22) Gehrke, N.; Cölfen, H.; Pinna, N.; Antonietti, M.; Nassif, N. *Cryst. Growth Des.* **2005**, *5*, 1317.

(23) Heywood, B. R.; Rajam, S.; Mann, S. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 735.

(24) Leeuw, N. H. d.; Parker, S. C. *J. Phys. Chem. B* **1998**, *102*, 2914.

charged CTAB can interact with negatively charged carbonate ions in the (110) faces, as many carbonates are coplanar with Ca atoms in this face.^{23,25,26} The surfactant adsorption suppresses crystal growth in the [110] direction. As a result, the calcite crystal develops into an elongated prismatic shape along the crystallographic *c* axis with exposed (110) faces. The adsorption of CTAB onto the calcite crystals was confirmed by thermogravimetric analysis (TGA). The TGA curve of calcite shows a decomposition peak around 400° C, which is consistent with the decomposition temperature of CTAB, suggesting that surfactant molecules remain strongly associated with the calcite crystals.

On the basis of the above analysis, we conclude that CTAB W/O microemulsions can mediate a well-defined condition for hexagonal vaterite crystal growth and its conversion to prismatic calcite. Cationic groups in some proteins and macromolecules may affect the biomineralization of calcite in ways similar to that observed with the CTAB microemulsion. Studies on microemulsions are helpful for developing chemically designed systems that mimic aspects of biomineralization to alter crystal morphology. Control of crystal morphology can prove beneficial for improving material properties and facilitating hierarchical assembly when inorganic crystals are used in technical applications. For example, the elongated shape of the calcite crystals can be exploited to align the particles when in suspension under flow or in an applied electric field. Figure 5 shows a colloidal suspension of the rod-shaped calcite in a fluorocarbon oil with an electric field applied as described previously.²⁷ The particles align and aggregate into chains that extend in the direction of the applied field. The aligned particles can thus potentially be used to fabricate anisotropic composite materials. The facile

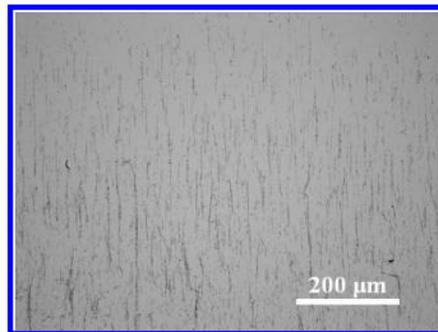


Figure 5. Optical microscopy image of rod-shaped calcite crystals suspended in fluorocarbon oil and aligned by an applied electric field. The crystals aggregate in particle chains that extend in the direction of the applied field.

degradation of calcium carbonate in acidic solution also makes it potentially useful as a template for controlling the structure of other materials. For example, silica nanotubes have recently been synthesized in our laboratory by growing silica around the calcite rods, then dissolving the calcite core in acid.

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Supporting Information Available: Experimental methods, XRD, FTIR, SEM, TEM, and TGA characterization procedures, XRD spectra of synthesized rhombohedral calcite particles in the control experiment in the absence of microemulsions, and TGA results of synthesized rhombohedral calcite, prismatic calcite, and CTAB. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(25) Mann, S.; Didymus, J. M.; Sanderson, N. P.; Heywood, B. R.; Samper, E. J. A. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1873.

(26) DeOliveira, D. B.; Laursen, R. A. *J. Am. Chem. Soc.* **1997**, *119*, 10627.

(27) Lin, J.-C.; Yates, M. Z.; Petkoska, A.; Jacobs, S. *Adv. Mater.* **2004**, *16*, 1944.