

## Effect of Magnesium Ions on Oriented Growth of Calcite on Carboxylic Acid Functionalized Self-Assembled Monolayer

Yong-Jin Han and Joanna Aizenberg\*

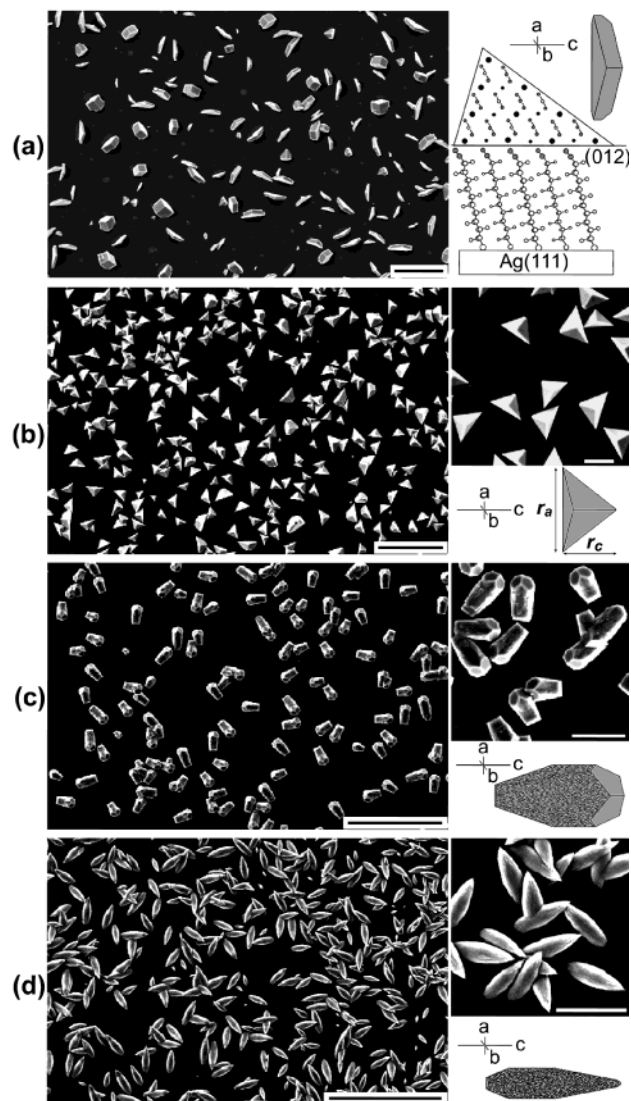
Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974

Received January 9, 2003; E-mail: jaizenberg@lucent.com

The development of chemical routes leading to controlled crystallization is an important requirement in the synthesis of crystalline materials for various applications. New synthetic approaches are often inspired by biology, which shows countless examples of biogenic crystals with finely tuned sizes, shapes, crystallographic orientation, polymorphs, etc.<sup>1</sup> In particular, the importance of calcium carbonates in nature has led to extensive studies of  $\text{CaCO}_3$  crystallization using two main bioinspired methods: (i) templating by structured organic surfaces,<sup>2–4</sup> such as self-assembled monolayers (SAMs), Langmuir monolayers, biomacromolecules, and functionalized polymers; and (ii) solution precipitation with growth modifiers,<sup>5–8</sup> such as ions, proteins, and synthetic polymers.  $\text{Mg}^{2+}$ , especially, has been studied extensively as an additive,<sup>5–7</sup> because  $\text{Mg}^{2+}$  ions are found in biological environments in high concentrations and are believed to play a critical role in the  $\text{CaCO}_3$  formation. Although these methods independently offered a certain level of control over crystal orientation, or polymorph and morphology, fine-tuning of the combination of these properties in one experiment has not been reported, and the crystals grown were often diverse in sizes and shapes within a single sample. Here we show that the combination of the above methods, templating and solution additives, provides control over multiple parameters of crystal nucleation and growth. Calcite crystals with uniform nucleating plane, shape, morphology, and size were synthesized for the first time, using carboxylic acid functionalized SAMs as templates and  $\text{Mg}^{2+}$  ions in solution as growth modifiers.

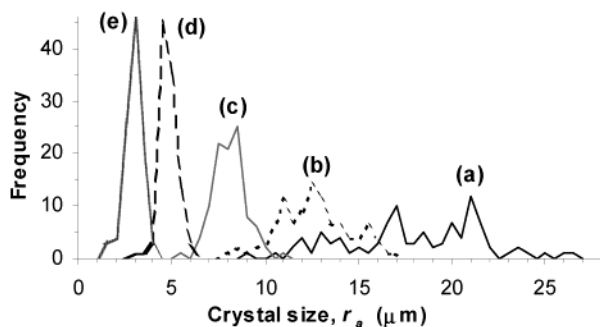
The template preparation for calcium carbonate deposition was performed as reported previously.<sup>2</sup> Briefly, a 15 nm-thick film of Ag (111) was evaporated on a Si (100) wafer primed with Ti as an adhesion promoter and exposed to a 5 mM solution of 11-mercaptopundecanoic acid in ethanol for at least 2 h. The resulting carboxylate-terminated SAM with an even number of methylene groups in the chain (MUA-SAM) was assayed for its ability to nucleate calcite for the first time. The templates were immersed in a 25 mM calcium chloride solution in a  $6 \times 4$  well-plate (well diameter = 1.5 cm), with the functionalized surface facing down to avoid collecting any solution-borne crystals. The crystallization was performed in a desiccator containing ammonium carbonate as the source of  $\text{CO}_2$  at room temperature for 2 h.<sup>2,5</sup>

Scanning electron microscopy (SEM) of the precipitates on MUA-SAMs showed densely nucleated arrays of calcite crystals of various sizes (Figure 1a). As deduced from the X-ray diffraction data morphological analysis<sup>9</sup> and computer simulations, calcite crystals were all normal {104} cleavage rhombohedra, nucleated homogeneously from the (012) crystallographic plane. The growth of calcite crystals on unfunctionalized silver or on methyl-terminated SAMs showed only randomly oriented calcite crystals with low nucleation density. The remarkable orientational specificity induced by MUA-SAM (~97–99% oriented crystals) can be attributed to the effect of aligned carboxylates on the surface of the SAM. The



**Figure 1.** SEMs of calcite crystals grown on MUA-SAMs. (a)  $m = 0$ ; (b)  $m = 0.5$ , (c)  $m = 1.5$ , (d)  $m = 2.0$ . Scale bars = 50  $\mu\text{m}$ . The insets present computer simulations of the morphologies of corresponding calcite crystals nucleated from the (012) plane (crystallographic axes are indicated). Also shown are the relative orientations of the MUA-SAM and calcite crystal it nucleates (in (a)), and zoomed SEM views (in (b–d)). Scale bars in insets = 10  $\mu\text{m}$ .

reported structural characteristics of SAMs on  $\text{Ag}^{10}$  suggest that the  $\text{CO}_2^-$  groups in the MUA-SAM are parallel to the  $\text{CO}_3^{2-}$  ions in the (012) plane of calcite (Figure 1a, inset). The carboxylates could, therefore, act as surrogate oxyanions for a nascent calcite nucleus, thus promoting the selective nucleation of calcite from the (012) plane.<sup>11</sup>



**Figure 2.** Size distribution of calcite crystals grown on MUA-SAM with (a)  $m = 0$ , (b)  $m = 0.5$ , (c)  $m = 1.0$ , (d)  $m = 1.5$ , and (e)  $m = 2.0$ .

To study the effect of additives on the templated calcite crystallization, magnesium nitrate was added to the calcium chloride solution in various concentrations  $m$  ( $m = \text{mol Mg}^{2+}/\text{mol Ca}^{2+}$ ). Examination of calcite crystals grown with Mg in the growth solution showed that Mg ions did not influence the selective nucleation of calcite from the (012) planes on MUA-SAMs, but did have a pronounced effect on crystal growth (Figure 1b–d). For  $m = 0$ –0.5, Mg induced a noticeable effect on the crystal size and shape distribution, which changed from largely random (Figure 1a) to more uniform {104} rhombohedra nucleated from the (012) plane (Figure 1b). A further increase in Mg concentration ( $m > 0.5$ ) resulted in highly controlled morphological modifications of calcite crystals. In addition to the normal {104} cleavage planes of calcite, these crystals exhibited striated faces with rough texture, slightly oblique to the  $c$ -axis (Figure 1c). Morphological analyses and computer simulations showed that these new faces formed an angle of 5–14° with the  $c$ -axis, which roughly corresponds to the {0 $k$ 1} family, where  $k = 1$ –3. The experiments with  $m > 1.5$  yielded needle (seed)-shaped crystals with uniform size, faceted only by the {0 $k$ 1} surfaces (Figure 1d). The crystals were elongated in the  $c$ -direction and formed an angle of 26° with the surface. The same seedlike calcite crystals were observed when  $m$  was increased up to 4, a ratio known to promote the formation of aragonite.<sup>6</sup>

Statistical analyses of calcite crystals<sup>9</sup> showed that the increase in the concentration of  $\text{Mg}^{2+}$  ions in the growth solutions considerably narrows the crystal size distribution (Figure 2). We observed a significant reduction in the crystal dimensions in the  $a,b$ -plane, with  $r_a$ 's of  $18.2 \pm 3.7$ ,  $12.6 \pm 1.9$ ,  $8.3 \pm 0.9$ ,  $4.9 \pm 0.3$ , and  $3.2 \pm 0.4 \mu\text{m}$  for  $m = 0, 0.5, 1.0, 1.5$ , and  $2$ , respectively, while the crystal sizes in the  $c$ -direction remained nearly constant ( $r_c \approx 8$ – $9 \mu\text{m}$ ). The relative sizes of the {0 $k$ 1} and {104} faces grew systematically with  $m$ . The EDX analysis also showed a gradual increase of  $\text{Mg}^{2+}$  concentration within calcite (up to 40 mol %  $\text{Mg}^{2+}$  for  $m = 4$ ). The mechanism of this high-level incorporation of  $\text{Mg}^{2+}$  within the synthetic magnesium-calcite crystals is currently being studied in detail.

Our results show that the formation of the new faces and the narrowing of the crystals size distribution can be attributed to the inhibition effect of the  $\text{Mg}^{2+}$  ions on the growth of calcite. Selective binding as partially hydrated  $\text{Mg}^{2+}$  ions<sup>6</sup> to the {0 $k$ 1} surfaces of calcite, which are nearly parallel to the  $c$ -axis, would systematically alter the crystal morphology and limit the crystal growth in the  $a,b$ -plane, thus promoting an asymmetric growth in the  $c$ -direction and ultimately yielding the uniform needle-shaped crystals (Figure 1d). Although analogous morphological changes in calcite crystals induced by Mg ions have been reported earlier,<sup>5,6</sup> no oriented nucleation has been observed, and the uniformity in the crystal sizes and shapes has generally not been high. We believe that the

remarkable homogeneity achieved in the current study results from the oriented nucleation. In the absence of the preferential orientation, the variation in diffusion of Mg (or other) ions to the same crystallographic planes of growing crystals, which are differently oriented on the substrate, would cause the uncontrolled asymmetry in the modified crystals. For crystallographically oriented nuclei, on the other hand, the ion diffusion and the ensuing crystal growth would be identical for all growing crystals, resulting in uniform, characteristic changes in crystal sizes and shapes, depending on the additive concentration.

We also noticed that calcite crystals appear to have preferential lateral alignment with each other and the substrate. Angles of 0°, 60°, 90°, and 120° between crystals were predominant. Among them, 0° and 90° were observed more frequently. It is conceivable that the frequency of 90° may be due to the substrate effect of Si (100), while the 60° and 120° may be due to the six-fold symmetry of Ag (111) used in our multilevel (Si-Ti-Ag-SAM-crystal) system. These preferential angles, inherently present in the substrate, might have translated into the crystals grown on the surface. The ways in which chemical and structural information is stored and translated through multilevel templates require further investigation.<sup>3</sup>

In summary, we have demonstrated the highly controlled synthesis of calcite with uniform nucleating plane, size, and morphology, by combining the MUA-SAM-induced oriented nucleation with the addition of  $\text{Mg}^{2+}$  ions to the growth solution. The ability to form a statistically significant number of homogeneous crystals makes this approach suitable for detailed studies of the mechanisms of the oriented nucleation and of the incorporation of the impurities into the crystals. We suggest, therefore, that the use of the templating by chemically modified surfaces together with specialized growth modifiers in the crystallizing solution is a promising chemical route to yield high-level control of multiple parameters of crystallization in one experiment, including crystal orientation, size, shape, polymorph, and stability.

## References

- (1) (a) Lowenstam, H. A.; Weiner, S. *On Biomineralization*; Oxford University Press: Oxford, 1989. (b) Mann, S. *Biomineralization – Principles and Concepts in Bioinorganic Materials Chemistry*; Oxford University Press: Oxford, 2001.
- (2) Aizenberg, J.; Black, A. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 4500–4509.
- (3) Travaille, A. M.; Donners, J.; Gerritsen, J. W.; Sommerdijk, N.; Nolte, R. J. M.; van Kempen, H. *Adv. Mater.* **2002**, *14*, 492–495.
- (4) (a) Belcher, A. M.; Wu, X. H.; Christensen, R. J.; Hansma, P. K.; Stucky, G. D.; Morse, D. E. *Nature* **1996**, *381*, 56–58. (b) Addadi, L.; Moradian, J.; Shay, E.; Maroudas, N. G.; Weiner, S. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2732–2736. (c) Archibald, D. D.; Qadri, S. B.; Gaber, B. P. *Langmuir* **1996**, *12*, 538–546. (d) Heywood, B. R.; Mann, S. *Chem. Mater.* **1994**, *6*, 311–318. (e) Berman, A.; Ahn, D. J.; Lio, A.; Salmeron, M.; Reichert, A.; Charych, D. *Science* **1995**, *269*, 515–518.
- (5) Albeck, S.; Aizenberg, J.; Addadi, L.; Weiner, S. *J. Am. Chem. Soc.* **1993**, *115*, 11691–11697.
- (6) Raz, S.; Weiner, S.; Addadi, L. *Adv. Mater.* **2000**, *12*, 38–42.
- (7) (a) Kitamura, M. *J. Colloid Interface Sci.* **2001**, *236*, 318–327. (b) Davis, K. J.; Dove, P. M.; De Yoreo, J. J. *Science* **2000**, *290*, 1134–1137.
- (8) (a) Falini, G.; Gazzano, M.; Ripamonti, A. *Chem. Commun.* **1996**, 1037–1038. (b) Gütjahr, A.; Dabringhaus, H.; Lacmann, R. *J. Cryst. Growth* **1996**, *158*, 310–315. (c) Falini, G.; Albeck, S.; Weiner, S.; Addadi, L. *Science* **1996**, *271*, 67–69. (d) Aizenberg, J.; Lambert, G.; Weiner, S.; Addadi, L. *J. Am. Chem. Soc.* **2002**, *124*, 32–39. (e) Naka, K.; Chujo, Y. *Chem. Mater.* **2001**, *13*, 3245–3259. (f) Meldrum, F. C.; Hyde, S. T. *J. Cryst. Growth* **2001**, *231*, 544–558.
- (9) A population of 100 crystals from a randomly selected area (viewed down the surface normal by SEM) was used in statistics for each experiment. We measured crystal sizes  $r_a$  and  $r_c$  in the  $a$  and  $c$  direction, respectively (see Figure 1b, inset), and angles between the crystal edges meeting at the upper corner of the crystal, which unequivocally define the nucleation plane.
- (10) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152–7167.
- (11) A comparative study of the effects of SAMs with odd and even chains on the oriented nucleation of calcite will be reported elsewhere.

JA034094Z